CSTC 2007

16th Canadian
Symposium on
Theoretical Chemistry

Le 16ième symposium
canadien de
chimie théorique

Memorial University
St. John's, Newfoundland and Labrador, Canada
August 4-9, 2007

Abstracts and Program

Welcome

We are pleased to welcome you to the 16th Canadian Symposium on Theoretical Chemistry, CSTC'2007. This year the CSTC is bringing together theoretical chemists from Canada and from around the world. We have invited speakers from Australia, Belgium, Canada, France, Germany, Hungary, India, Sweden, the U.K. and the U.S.. Our program, consisting of invited speakers and contributed posters, covers a broad range of theoretical and computational chemistry. We are especially pleased by the large number of participants from Atlantic Canada.

This is the first time the CSTC is held in the province of Newfoundland and Labrador. We hope that you will take advantage of this opportunity to visit St. John's, the oldest city in North America, and one of the most picturesque province of Canada.

We are very grateful to the Dean of Science of Memorial University, the Dean of Science of the University of Calgary, an anonymous donor, ACEnet and Gaussian Inc. for their financial support.

We would like to thank Dr. Erika Merschrod for her work with our web page and organizing the conference abstracts and Chris Flinn for his help. We are especially grateful to Mary Flinn for her hard work and support.

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General Information (compliments of Mrs. Kathy Mackey)

Welcome to the oldest and most easterly city in North America.
Where to visit, What to see and buy, and Where to eat in St. John's

PLACES TO VISIT:

NEWMAN VAULTS – 436 Water St. Sundays and Mondays only. Starts at 8:30pm. $10.00 per person, tickets at the door. Here you will taste the famous Newman Port, have a bit of cheese and fruit and enjoy a play. Two billings: "Rats in The Wall" and "Cask of Amontillado". Make sure you wear sneakers or walking shoes, the floor is uneven and the place is only lit by candles. It is also cool inside, so take a sweater or jacket.

HAUNTED WALK – meet at the West entrance of the Anglican Cathedral at 9:30pm I believe the fee is $5.00 per person and they collect it on the spot. Wear walking shoes and take a sweater. Sundays and Mondays: "Sinners and Spirits" tour Tuesdays, Wednesdays and Thursdays: "Ghosties and Ghoulies" tour

QUIDI VIDI BREWERY AND VILLAGE – drive down to Quidi Vidi Village and park close to Mallard Cottage. Walk to the micro Brewery. You could possibly drive, but it is very hard to turn around, especially if there are other cars. Go on a beer tour. Then walk further and see the village and historic sites. On the way back, visit Mallard Cottage, just for fun, it is full of "stuff" and it is supposed to be the oldest building in St. John's. Quidi Vidi Village is where Farley Mowat's "A Whale For The Killing" was filmed.

THE ROOMS – open from 10am to 5pm Mondays and Saturdays. 10am to 9pm on Wednesdays and Thursdays and Sundays noon to 5pm. Entrance fee $5.00 but free from 6pm to 9pm on Wednesdays. It is an art gallery, museum and much about the history of the Island. Do this on a rainy day, although the view from the top floor is spectacular. It's easy to spend half a day here, so plan to have lunch in the small restaurant. Food is simple, but very good and reasonable.

PRESENTATION SISTER'S CONVENT – next door to the Catholic Basilica. Open weekdays only, 10:30am till 12:00 noon and 2:00 to 4:00pm Statue of the "Veiled Virgin" by Giovanni Strazza. This is very much worth your while to see, it is a most incredible statue. No fee, but a donation is welcomed/expected.

LOWER BATTERY – just a walk around the bottom part of Signal Hill. Leave the car close to the Fairmont Hotel because the streets are very narrow and it is really hard to get around. Walk towards Signal Hill, and turn right at Lower Battery Road. There are several forks in the road as you walk, but keep to the right, close to the water till you get to Outer Battery Road at the end. There are very old homes on both sides of the street, built right into the rocks. Take a camera and binoculars. Expect at least 2-3 hours. Go on a clear, preferably not windy day. (There are small paths going uphill as well, so if you are a good hiker, you can go up to Cabot Tower from here. In that case expect to spend the whole day, so take lunch.)

FORT AMHERST – this is on the South Side of the Harbour. Drive only as far the sign tells you to. Walk the rest of the way, to the Light House. Take camera and binoculars, you might see whales and icebergs. When the Light House is right in front of you, look to your right at the rocks, just a little up and about 150 yards out. There are 3 graves. Sailors are buried there from a time when passing ships were looking for a place to bury their dead. Choose a warm, clear day for this walk.

SIGNAL HILL – Drive up to the top and park. Visit Cabot Tower – open daily from 8:30am to 9:00 pm – and go up into the tower. Take camera and binoculars. If you are a good walker, go on a hike, expect it take at least 2-3 hours. Go on a nice day, this is a very windy place.

INTERPRETATION CENTRE – halfway up Signal Hill on the right. No charge. Open daily from 10:00am till 6:00pm.

JOHNSON GEOCENTRE – half way up Signal Hill on the left. $ 8.00 per person and open Mondays to Saturdays 9:00am to 5:00pm and Sundays 1:00pm to 5:00pm.
This is an interpretation center about the rocks and formation of Newfoundland and the Earth. A very worthwhile, interesting place. Go on a rainy day.

DEVON HOUSE CRAFT CENTRE – directly across the street from The Fairmont on Duckworth St. This is the place to buy gifts and Newfoundland handicrafts. All locally made and the prices are well within the range anywhere in the City. Also go upstairs to the Gallery. This is a nice place to visit even if you are not shopping.

THE FOUR SISTERS – on Temperance Street. (Come east on Duckworth St., just past the Devon House Craft Centre. Temperance is the first street on your right.) There are four identical houses. The man who built Cabot Tower, built these four houses for his daughters. (From the rocks he ordered from Ireland to build the Tower?) There is a tunnel connecting the houses so his daughters did not have to come out onto the street to visit each other.

CAPE SPEAR – about 11km outside of St. John's. Take Water St. going West. Cross the small bridge on the left going to the South Side. Keep on the road all the way to the end. There is a good interpretation Centre, and a visit to the Light House is very worth while. It is kept in the period it was used in. It's a fairly good walk, could be very windy, take camera and binoculars. Whales are often seen. Also, if you go there early in the morning, specially with breakfast in hand, you might have a silver fox come and visit you.

WHALE WATCHING – drive to Bay Bulls (about 1 hour) and take a tour boat. Cost is about $60.00 per person and takes about 2.5 hours. We like O'Brien's the best, but others are good too. Take sweater, camera and binoculars.

BELL ISLAND – you have to take the ferry from Portugal Cove to get there. Take tours of the old coal mines (very interesting), visit the light house, walk the beaches. There are a couple of little greasy spoon restaurants, but I much prefer to take a picnic basket and eat on the beach. It is best to leave in the morning and return late afternoon.

Saturday, August 4 Inco Innovation Centre, Room IIC2001

12:00 noon	Afternoon registration
7:00 p.m.	Welcome reception

Sunday, August 5th

8:45 a.m.	Welcome
Sunday Sessions	
Session I	Chair: Dennis Salahub
9:00	*Title: "Superconductivity in High Pressure Solids - A Chemical Prespective"* **John Tse, Department of Physics and Engineering Physics, University of Saskatchewan**
9:45	*Title: "New Stochastic Approaches to the Electron Correlation Problem"* **Alex Thom, Department of Chemistry, University of Cambridge**
10:30	Coffee Break
Session II	Chair: Peter Kusalik
11:00	*Title: "Event-Driven Simulations using Energy Discontinuities"* **Jeremy Schofield, Chemical Physics Theory Group, University of Toronto**
11:45	*Title: "From Transition Paths to Transition States, Reaction Coordinates, and Reaction Rates"* **Gerhard Hummer, Laboratory of Chemical Physics, NIDDK, National Institutes of Health**
12:30 - 2:00	Lunch Main Dining Hall (Tickets provided)
2:00	Poster Session A - IIC Atrium upper and lower level
Session III	Chair: Phil Bunker
3:15	*Title: "Combining the Advantages of an Iterative Eigensolver and a Contracted Basis to Compute Energy Levels of* CH_5^+*"* **Tucker Carrington, Département de chimie, Université de Montréal**
4:00	Coffee Break
4:30	*Title: "Pulse Shaping for the Optimal Control of Molecular Excitation"* **Alex Brown, Department of Chemistry, University of Alberta**
5:15	*Title: "Carbon-Carbon Bond Breaking: The Beta-Scission Problem"* **Allan East, Department of Chemistry, University of Regina**

Monday, August 6th Inco Innovation Centre, Room IIC2001

Monday Sessions	
Session IV	Chair John Goddard
9:00	*Title: "Geometric Structure of Clusters: Global Optimization and Structural Principles"* **Rene Fournier, Department of Chemistry, York University**
9:45	*Title: " Stochastic Methods for the Study of Structure and Dynamics in Chemistry"* **Jim Doll, Department of Chemistry, Brown University**
10:30	Coffee Break
Session V	Chair: Gilles Peslherbe
11:00	*Title: "Dynamics of Quantum Fluids: Path Integral and Semiclassical Methods"* **Nancy Makri, Department of Chemistry, University of Illinois at Urbana-Champaign**
11:45	*Title: "Chemical Reaction Rates from Ring Polymer Molecular Dynamics"* **David Manolopoulos, Department of Chemistry, Oxford University**
12:30 - 2:00	Lunch Main Dining Hall (Tickets provided)
2:00	Poster Session B - IIC Atrium upper and lower level
Session VI	Chair: Paul Mezey
3:15	*Title:"Convergence, Chaos and Divergence: Stability Analysis of Iterative Procedures in Quantum Chemistry"* **Peter Surjan, Laboratory of Theoretical Chemistry, Eötvös University**
4:00	Coffee Break
4:30	*Title: "Conceptual Density Functional Theory: Applications in Pericyclic and Redox Reactions"* **Paul Geerlings, Faculty of Science, Free University of Brussels**
5:15	*Title: "Model Hamiltonians in Electronic Density Functional Theory"* **Paola Gori-Giorgi, Laboratoire de Chimie Théorique, Université Pierre et Marie Curie**
6:00 - 6:30	CATC Business meeting

Tuesday, August 7th Inco Innovation Centre, Room IIC2001

Tuesday Sessions	
Session VII	Chair: Stacey Wetmore
9:00	*Title: "Border Region Treatment for Fragment-Based Quantum Chemical and Mixed Quantum Mechanical / Molecular Mechanical Approaches"* **Thomas E. Exner, Fachbereich Chemie, Universität Konstanz**
9:45	*Title: "Theoretical and Computational Approaches to the Chemistry of Alzheimer's Disease"* **Arvi Rauk, Department of Chemistry, University of Calgary**
10:30	Coffee Break
Session VIII	Chair: Alain St. Amant
11:00	*Title: "Simulations of Peptide Aggregation:* **Joan-Emma Shea, Department of Chemistry and Biochemistry, University of California Santa Barbara**
11:45	*Title: "Towards a new generation of force fields for predictive hierarchical multiscale molecular modelling"* **Aatto Laaksonen, Division of Physical Chemistry, Arrhenius Laboratory, Stockholm University**
	FREE Afternoon

Wednesday, August 8th Inco Innovation Centre, Room IIC2001

Wednesday Sessions	
Session IX	Chair: Igor Svishchev
9:00	*Title: "Dynamical Heterogeneity and Violation of the Stokes-Einstein Relation in Glass-Forming Liquids"* **Peter Poole, Department of Physics, St. Francis Xavier University**
9:45	*Title: "Dynamics of Organization at the Nanometer Scale"* **Phillip Geissler, Department of Chemistry, University of California Berkeley**
10:30	Coffee Break
Session X	Chair: Galina Orlova
11:00	*Title: "Probing Condensed Phase Electronic Structure and Dynamics with Mixed Quantum-Classical Simulation"* **Peter Rossky, Department of Chemistry and Biochemistry, University of Texas at Austin**
11:45	*Title: "Charge Solutes in Hydrogen Bonded Systems: Solvation Characteristics, Dynamics and Ultrafast Vibrational Spectroscopy"* **Amalendu Chandra, Department of Chemistry, Indian Institute of Technology**
12:30	Lunch Main Dining Hall (Tickets provided)
2:00	Poster Session C - IIC Atrium upper and lower level
Session XI	Chair: Mariusz Klobukowski
3:15	*Title: "First Principles Simulations of Nanostructures and Confined Liquids"* **Giulia Galli, Department of Chemistry, University of California, Davis**
4:00	Coffee Break
4:30	*Title: "Density-Functional Study of Peierls Instability in Carbon Nanotubes Using Hybrid Functionals"* **Michel Côté, Département de Physique, Université de Montréal**
5:15	*Title: "How Does Trimethylamine-N-oxide Counter Urea-Induced Protein Denaturation?"* **Gren Patey, Department of Chemistry, University of British Columbia**
7:00 - 10:00	Banquet (Tickets required) - dinner at 7:30

Thursday, August 9th Inco Innovation Centre, Room IIC2001

Thursday Sessions	
Session XII	Chair: Paul Ayers
9:00	*Title: "Electron Correlation Through the Lens of the Ω Intracule"* **Peter Gill, Research School of Chemistry, Australian National University**
9:45	*Title: "Recent Developments in State-Specific Multi-Reference Coupled Cluster Theory and its Approximants"* **Debashis Mukherjee, Department of Physical Chemistry, Director, Indian Association for the Cultivation of Science**
10:30	Coffee Break
Session XIII	Chair: James Gauld
11:00	*Title: "Packing and Dynamics in Hard Core Particle Systems"* **Richard Bowles, Department of Chemistry, University of Saskatchewan**
11:45	*Title: "Tracer Diffusion: New Answers to Old Questions"* **Mark Thachuk, Department of Chemistry, University of British Columbia**
12:30	Conference ends

Poster Session A – Sunday

No.	*Presenter*	*Title of Presentation*
A-1.	Hakima Abou-Rachid	Quantum mechanical theoretical analysis of newly-synthesized energetic compounds based on fused-1,2,4-triazine heterocycles
A-2.	Mansour Almatarneh	Mechanisms for the deamination reaction of cytosine with H_2O/OH^- and $2H_2O/OH^-$: A computational study
A-3.	H. J. Bohorquez	Quantum Molecular Similarity: an Atoms in Molecules Approach.
A-4.	Richard K. Bowles	Freezing in Gold Nanoparticles.
A-5.	P.J. Bruna	Quadrupole, Octopole and Hexadecapole Moments of Σ, Π, Δ and Φ States. Cylindrically Asymmetric Charge Density Distributions in Linear Molecules with Nonzero Electronic Angular Momentum
A-6.	Valérie Campagna-Slater	PSMC: A novel protein loop modelling algorithm using Preferential Sampling and Monte Carlo refinement
A-7.	Norberto Castillo	Are sugars quantum?
A-8.	Shaheen Fatima	H-doping effects on surface states of ZnO nanoparticles
A-9.	Melissa Gajewski	DFT calculations on the electronic structure and geometry of EDTA and its complexes with $\mathbf{Mg^{2+}}$, $\mathbf{Ca^{2+}}$, $\mathbf{Sr^{2+}}$, $\mathbf{Na^{+}}$, $\mathbf{K^{+}}$, and $\mathbf{Rb^{+}}$ cations
A-10.	Bin Gao	First Principle Simulations of Nano-Diamondoids and Semiconducting Single-Walled Carbon Nanotubes
A-11.	Kelsie Gillies	Ionization of Basic and Aromatic Amino Acids: A Theoretical Study
A-12.	John D. Goddard	Predictions of the Fluorescence Emission Energies of Oxyluciferins: Solvent Effects.
A-13.	Zhijun Gong	Theoretical Studies of the Electronic and Optical Properties of Fluorene-Based Conjugated Copolymers
A-14.	Francois Goyer	Using complex potentials to calculate electron transmission in molecules.
A-15.	Fritz Grein	Density functional theory applied to excited states.
A-16.	Robbie Grunwald	Decoherence and quantum-classical master equation dynamics
A-17.	Anna V. Gubskaya	Machine-Learning Models in Computer-Aided Discovery of Biodegradable Polymers
A-18.	Minwoo Han	Influence of molecular geometry and intra-aggregate forces on shapes of self-assembled amphiphilic molecular dumbbells

Poster titles

A-19.	Nadine S. Hewitt	Amino acid based models for lead-protein binding
A-20.	Shahidul M. Islam	A Comparison of the Performance of the Standard 6-31G and the Binning-Curtiss Basis Sets for 3rd Row Elements
A-21.	Dale Keefe	Computational Study of a Chloroform-Benzene-Chloroform Complex
A-22.	Evan Kelly	QM/MD simulations of Vinca Alkaloid drugs
A-23.	A Kelly	Dynamical suppression of decoherence using nonideal laser pulses.
A-24.	Heeyoung Kim	Sequence Dependent Coherence Variation in DNA Charge Transfer processes
A-25.	Lin Ling	DFT Study of Band Structure on PA and OLED Materials
A-26.	Jaime M. Martell	Computational study of the use of naphthalimide derivatives as photosensitizers for selective oxidation of guanine in DNA
A-27.	Dennis Salahub	DNA-dependent RNA polymerases: Common structures of the active sites and possible reaction mechanisms

Poster Session B – Monday

No.	*Presenter*	*Title of Presentation*
B-1.	Minwoo Han	Carbon-hydrogen bond activation mechanism of aldimine by Rhodium(I) catalyst
B-2.	Lisandro Hernández de la Peña	Computation of the Formation Free Energy of Ionic Aqueous Clusters: Equilibrium vs. Non-equilibrium Methods
B-3.	Joshua W. Hollett	Simulated Electronic Structure Calculation Approach to Molecular Mechanics
B-4.	Shahidul M. Islam	New Insights into the Kinetics of the Reaction of Ethene + Bromine -A Computational Study
B-5.	Heeyoung Kim	Coherent excitation energy transfer within meso-meso linked Zn(II) porphyrin array with 5,15-bisphenylethynylated porphyrin acceptor
B-6.	O. Kravchenko	Tracer Diffusion in Rough Sphere Fluids
B-7.	Xiangzhu Li	Reduced multireference CCSD and CCSD(T) methods for quasidegenerate states. Theory and some applications
B-8.	Yaping Li	Electric Field Effects on Bipolaron Transport in Polythiophene
B-9.	John M. H. Lo	The DFT studies of the formation of C_2 hydrocarbons on the Fe(100) surface
B-10.	Matthew MacLennan	Fragmentation and Proton Transfer Mechanisms of Radical-Cationic Tryptophan: A Theoretical Study
B-11.	G. Madhurambal	Growth and characterization of Tutton salts
B-12.	Sergei Manzhos	Neural network-based methods for fitting multidimensional potential surfaces and computing wavefunctions
B-13.	Shane McCarthy	A non-local Wigner-like correlation energy density functional: Parameterization and tests on two-electron systems
B-14.	Alaina McGrath	Do added water molecules break the strong hydrogen bonds in the formic acid dimer?
B-15.	Nicole McNeil	Ionization of Gaseous Aliphatic Amino Acids: A Theoretical Study
B-16.	Heidi M. Muchall	Experimental and computational NMR studies on the interplay of weak interactions in RNSO·pyridine complexes
B-17.	Istok G. Nahtigal	Nucleation of NaCl nano-particles in supercritical water: A Molecular Dynamics study

Poster titles

B-18.	Yu-ya Ohnishi	Post Hartree-Fock calculation with one-electron model atom: Application to large transition metal complexes
B-19.	Galina Orlova	Competitive Proton-Transfer and Electron-Transfer Dissociations of Ternary Cu(II)-Histidine Complexes.
B-20.	Jason K. Pearson	Insight into the Catalytic Activity of Selenium-Containing Antioxidants
B-21.	Gilles H. Peslherbe	Role of Polarization in Simulations of Excited-State Dynamics: $NaI(H_2O)_n$ Photodissociation as a Case Study
B-22.	Andriy Plugatyr	Spatial Hydration Structures of Aromatic Molecules in Ambient and Supercritical Water
B-23.	Michael Probst	Dissociative Electron Attachment to Biomolecules
B-24.	Georg Schreckenbach	Uranyl Hydroxide
B-25.	A. St-Amant	Implementation of an Extremely Fast and Linear Scaling Xα Algorithm
B-26.	Yan Sun	Density functional study of 13-atom clusters of second row transition metals
B-27.	Min Zhang	Global optimization of 13-atom 5d transition metals

Poster Session C – Wednesday

No.	*Presenter*	*Title of Presentation*
C-1.	Shahidul M. Islam	A new insight into using chlorine leaving group and nucleophile carbon kinetic isotope effects to determine substituent effects on the structure of S_N2 transition states
C-2.	Heeyoung Kim	Environment Dependent Coherence of a Short DNA Charge Transfer System
C-3.	P. Rocheleau	Establishing a link between molecular polarizabilities and molecular conductance
C-4.	D. Rozmanov	Temperature dependence of ice growth from computer simulations
C-5.	Georg Schreckenbach	DFT Study of Polypyrrolic Macrocycles: Analysis of Actinyl-Oxo-to-Transition-Metal Bonding
C-6.	Markus Schröder, Jose-Luis Carreon-Macedo	Molecular Quantum Computing Using The Multi-Configuration Time-Dependent Hartree Approach
C-7.	Brad Scott	Micro-solvation of glycolic acid: Intramolecular and intermolecular hydrogen bonding
C-8.	Dawn M. Shaw	Characterization of Hydrogen Bonding of Water Under Extreme Conditions: Insight From Electronic Structure Calculations
C-9.	É. Simon	Novel Boron-Nitrogen Nano-Needles: Geometry, Electronic Structures and Application of the Nuclear Charge Convexity Theorem
C-10.	A. St-Amant	Adaptive Semi-Empirical Importance Functions for Monte Carlo Simulations
C-11.	Mark S. Staveley	Computing Numerical Hessians in Parallel
C-12.	Yan Sun	Geometric and electronic structure of closed-shell bimetallic A_4B_{12} clusters
C-13.	Ágnes Szabados	Comparison of some multireference perturbation theories at ground and excited states
C-14.	Cs. E. Szakacs	A novel group of molecules: hydrogenated and nonhydrogenated BN angular helices. A theoretical study
C-15.	Alexis Taylor	Investigation of Quadruplex DNA Structures Using the Theory of Atoms in Molecules
C-16.	Qadir K. Timerghazin	Fluorescent proteins: Benchmarking computational methods against new experimental measurements

Poster titles

C-17.	Tereza Varnali	Role of frontier orbitals in mixed valent trinuclear complex ions
C-18.	Surajith N. Wanasundara	Theory Behind the Charge Distribution on Dissociated Protein Complexes in the Gas Phase
C-19.	S. D. Wetmore	Characterization of Weak Interactions between Aromatic Amino Acids and Natural or Damaged DNA Nucleobases
C-20.	Sarah R. Whittleton	Investigating the Monomer-Dimer Equilibria of Acyclic and Cyclic Stannylene Acetals
C-21.	Stephanie Y. Wong	Implementation of *Ab initio* Molecular Dynamics in the Molecular Modelling Toolkit
C-22.	Koichi Yamashita	Efficient ab initio Method for Electron Transport and Nonadiabatic Interactions in Molecular Junction/Interfaces
C-23.	Ryan R. Zaari	Targeted vibrational excitation of ClO: Optimal control theory and genetic algorithm results
C-24.	Tao Zeng	The Role of Covalency in AuXe^+ system
C-25.	Min Zhang	Global optimization of AuN (N=16,32) clusters

Oral Presentation Abstracts

Superconductivity in High Pressure Solids – A Chemical Perspective

J.S. Tse*, Y. Yao
Department of Physics and Engineering Physics, University of Saskatchewan

The structural principle behind the unusual features in the high pressure phases of simple alkali elements is reviewed. It is shown that there exists a pressure regime where the elemental solids are likely to adopt a layer structure. There are two novel characteristics associated with this structure type. The system tends to be at the proximity of phonon and electronic instabilities. The combined effect is significant enhancement of electron-phonon coupling and resulting in a superconducting state. We demonstrate this empirical observation with selected examples including a recently predicted novel structure of high pressure SnH_4 which shows very high superconducting critical temperature. Recent results on ab initio prediction of high pressure crystal structures, particularly those with superconductivity behaviour will be presented.

New stochastic approaches to the electron correlation problem

Alex J. W. Thom*, Ali Alavi
Department of Chemistry, University of Cambridge

The concept of a 'graph', consisting of a set of connected Slater determinants, gives us a new starting point for calculating the correlated electronic energy of molecules, which can be expressed as a sum over graphs†.

We show two different formulations of a graph sum:

1) Based on the path-integral formulation of quantum mechanics, graphs contain contributions from resummations of exponentially large numbers of paths.

2) A reformulation of an arbitrary order of Möller-Plesset perturbation theory in terms of graphs.

Both formulations have the advantage that electronic energies can also be evaluated by stochastically sampling graphs which, crucially, can be generated with a known normalized generation probability; these stochastic methods can significantly reduce the scaling of calculations with system size.

This approach is free from fixed-node type approximations, and shows no significant 'minus-sign problems'. Our formulation is not system-dependent and we show correlated calculations on both molecular and periodic systems.

† *J. Chem. Phys.* **123**, 204106 (2005)

Event-Driven Simulations Using Energy Discontinuities

Jeremy Schofield*, Ramses van Zon
Chemical Physics Theory Group, University of Toronto

A scheme for performing event-driven, asynchronous simulations will be outlined that makes use of discretizations of a continuous potential and the exact solution of free motion of asymmetic bodies. The method is illustrated for constrained and rigid systems interacting via orientationally-dependent point potentials. Event-driven simulations will be contrasted with simulations based on elegant new symplectic integration schemes for rigid systems interacting by more conventional continuous potentials.

From transition paths to transition states, reaction coordinates, and reaction rates

Gerhard Hummer*, Robert B. Best
Laboratory of Chemical Physics, NIDDK, National Institutes of Health

Molecular mechanisms of reactions in condensed phase are reflected in their transition-state ensemble and transition paths. By exploiting a Bayesian relation between the phase-space distributions in the equilibrium and transition-path ensembles, the splitting or commitment probability, and the reaction rates, one can (1) identify transition states, (2) optimize reaction coordinates, and (3) estimate rate coefficients of rare molecular reactions. The general theory will be illustrated with applications to collective water dynamics as well as protein conformational transitions and folding.

Combining the advantages of an iterative eigensolver and a contracted basis to compute energy levels of CH_5^+

Tucker Carrington Jr*, Xiao-Gang Wang
Universite de Montreal, Chemistry Department

The vibrational spectrum of CH_5^+ is extremely difficult to compute, in part because the Schrödinger equation one must solve is 12-dimensional and in part because the five protons move almost freely around the carbon centre. I shall review a new method for using contracted basis functions in conjunction with the Lanczos algorithm to calculate vibrational energy levels and discuss its application to CH_5^+. As basis functions we use products of eigenfunctions of reduced-dimension Hamiltonians obtained by freezing coordinates. The basis functions represent the desired wavefunctions well, yet are simple enough that matrix-vector products may be evaluated efficiently. For CH_5^+ we solve a 7-dimension bend problem and a 5-dimension stretch problem and then compute levels of CH_5^+ using a basis of products of solutions of the bend and stretch problems. The basis we use is orders of magnitude smaller than that of the primitive product basis of $\sim 10^{12}$ functions. Converged excited state wavefunctions and energies are obtained using the symmetry-adapted Lanczos method.

Pulse shaping for the optimal control of molecular excitation

Alex Brown*, Markus Schröder
Department of Chemistry, 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 introduce some of the theoretical/computational research directions being pursued in my laboratory using optimal control theory (OCT) to determine the tailored laser pulses needed to achieve control. Within OCT, the dynamics of the system, given an initial state, is controlled in such a way that a given final state – the control target – is reached after a certain amount of time. A number of numerical schemes, most of them of iterative character, have been proposed to obtain the optimal laser pulse required to achieve this transformation. However, as these schemes involve numerically demanding forward and backward propagations of the initial and target states, one is limited to the treatment of small systems with a few (3-6) degrees of freedom. I will outline our use of the Multi-Configurational-Time-Dependent-Hartree (MCTDH) method for solving the time-dependent Schrödinger equation

Carbon-Carbon Bond Breaking: the Beta-Scission Problem

Allan L. L. East*
Dept. of Chemistry and Biochemistry, University of Regina

In catalytic cracking of hydrocarbons, the most common carbon-carbon bond-breaking step is thought to be beta scission of carbenium ions. However, for unbranched alkyl ions, beta scission would lead to a hypothetical primary carbenium ion, an isomer that has never been observed. My group has used traditional geometry optimizations and ab initio molecular dynamics (AIMD) to explore the question, "What is really happening during cationic beta scission?" This 3-year journey has investigated several related issues, such as protonated-cyclopropane structures and catalyst effects. Computational chemistry has revealed some interesting possible solutions to the beta scission problem, which will be shown.

Geometric Structure of Clusters: Global Optimization and Structural Principles

René Fournier*, Min Zhang, Yan Sun
Physics, York University

The structures of small clusters are mostly unknown and hard to predict because, unlike organic molecules for which we have Lewis theory, VSEPR, etc..., no simple model works for all clusters. I will review some likely global minimum structures of metal clusters that we found by global optimization (taboo search) on DFT energy surfaces. Structures of different clusters can be rationalized with different principles, such as "minimizing surface area", "minimizing differences in atomic coordinations", etc. I will give examples to illustrate which structural principles apply to which cases. In particular we see these tendencies: (a) elements that have a large ionization energy tend to form cluster structures where all atoms have nearly equal coordinations; (b) clusters of elements in groups 1, 2, 11, 12 and 13 generally have shapes consistent with the predictions of the jellium model; (c) the pair distance distribution function is broader in clusters of transition metal elements. These and other observations can help in the elucidation of cluster structure with limited experimental and computational data. I will also show examples of metal clusters that have special stability because they have a number of nuclei and electrons that match so-called "magic numbers", and the nuclear positions have a shell structure. Some of these clusters have calculated HOMO-LUMO gaps as large as 2.4 eV which is very unusual for metal elements.

Stochastic Methods for the Study of Structure and Dynamics in Chemistry

J. D. Doll*, D. L. Freeman
Department of Chemistry, Brown University

We consider a range of developments in the theory and application of stochastic methods. While focused on methods of particular interest in chemistry, the techniques discussed will be general-purpose in nature and broadly applicable to a range of both classical and quantum tasks. A number of applications will be examined, including examples taken from the study of cluster and extended systems. Recent developments in equilibrium and dynamical path integral methods will be reviewed.

Dynamics of quantum fluids: path integral and semiclassical methods

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The interplay of many-body nonlinear interactions and quantum mechanical effects such as zero-point motion or identical particle exchange symmetries lead to intriguing phenomena in low-temperature fluids, some of which remain poorly understood. Recent advances in theory and methodology have established the framework that has recently enabled the simulation of time-dependent processes in such systems. This lecture focuses on the formulation of forward-backward semiclassical dynamics (FBSD), a rigorous and efficient methodology for capturing quantum mechanical effects in the time evolution of condensed phase systems through classical trajectory information, and its application to low-temperature fluids. FBSD expressions for time-dependent expectation values or correlation functions take the form of phase space integrals with respect to trajectory initial conditions, weighted by the coherent state transform of a corrected density operator. Full quantization of the initial density is feasible by employing the discretized path integral representation of statistical mechanics, thus ensuring a proper treatment of zero point energy and identical particle exchange effects, while capturing important imaginary components. The FBSD approximation satisfies the detailed balance property of time autocorrelation functions and reverts to the exact quantum mechanical result at zero time. FBSD simulations have been performed to investigate the dynamics of low-temperature fluids, ranging from the nearly-classical supercritical argon to highly quantum mechanical systems such as liquid para-hydrogen and superfluid helium. The results of these calculations are in very good agreement with experimental results on diffusion coefficients and dynamic structure factors probed by neutron scattering. The FBSD simulations provide novel insights into the separate roles of quantum mechanical and quantum statistical effects on the dynamics of these fluids.

Chemical reaction rates from ring polymer molecular dynamics

David E Manolopoulos*, Rosana Collepardo-Guevara and Ian R. Craig
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This talk will review the ring polymer molecular dynamics theory of chemical reaction rates [J. Chem. Phys. **122**, 084106 (2005); **123**, 034102 (2005)], and present some new results of the theory for a model of proton transfer between a weak acid (phenol) and a weak base (trimethylamine) in an aprotic polar solvent (methyl chloride).

Convergence, Chaos and Divergence: Stability Analysis of Iterative Procedures in Quantum Chemistry

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Practically all quantum chemical methods involve some kind of iterative procedures, cf. the Hartree Fock (HF) model or the coupled-cluster (CC) technique. Even a simple eigenvalue problem, if the size of the matrix is large, is usually solved by iterative techniques, and perturbation theory, which is often considered as a noniterative approximation, can also be viewed as an iterative approach to the solution of the Schrödinger equation.

Analysis of convergence properties of general iteration schemes can be based on the associated Ljapunov exponents which all have to be negative to facilitate convergence. We study the nature of the fixed points of various iteration schemes, and demonstrate that on the borderline of convergence and divergence, quantum chemical iterations may also produce chaotic patterns. We shall mainly focus on the CC equations using the CC Jacobian to derive critical exponents, which can be tuned by selecting level shift parameters appropriately, permitting one to enforce convergence even in difficult cases. Another target of our investigation will be the idempotency-conserving iteration scheme for the HF density matrix, $P^{n+1} = P^n + \eta P^n F(1 - P^n)$, proposed recently to avoid explicit matrix diagonalization for large molecules, for which the appropriate choice of parameter η was found to be crucial to avoid divergence or chaotic behavior.

Conceptual Density Functional Theory: Applications in Pericyclic and Redox Reactions

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Conceptual Density Functional Theory [1,2,3] provides the chemists with sharp definitions of traditional chemical concepts (electronegativity, hardness, softness) thus ensuring their computability and their quantitative use as such or within the context of principles such as the electronegativity equalization principle, the Hard and Soft Acids and Bases principle. When applied to chemical reactivity until now most attention has been devoted to the case of (generalized) acid-base reactions with particular attention to the application of the HSAB principle both at global and local level [3][4]. In this contribution we concentrate on the possibility to reformulate the Woodward Hoffmann rules [5] for pericyclic reactions in terms of the electron density and associated DFT based reactivity descriptors; thus bypassing the need for the phase of the wave function. The initial hardness response [6] and the recently introduced dual descriptor [7] turn out to offer valuable alternatives [8] as shown in the case of simple cycloaddition and electrocyclization reactions. In the second part the redox behaviour of a species, as quantified by the redox potential, is linked to DFT descriptors such as electrophilicity, nucleofugality and electrofugality [9]. Applications are given both in the case of simple $Me^{n+}/Me^{(n-1)+}$redox couples, Me being a first row transition metal [10] and in the case of the interpretation of the redox potentials of bromo-, chloro- and nitro-oxo acids in gasphase and aqueous solution [11].

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Model hamiltonians in electronic density functional theory

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Electronic density functional theory within the formalism of Kohn and Sham uses a specific (model) hamiltonian which highly simplifies the many-electron problem to that of noninteracting fermions. To obtain the energy, or other properties of the real system, approximations for the exchange-correlation functional are needed. This complicated functional is determined by the spherically and system-averaged pair density (APD) along the so-called adiabatic connection. We have developed a formalism in which realistic APD are generated from simple unidimensional equations, to be solved for each system and eventually coupled to the Kohn-Sham ones. Physically motivated approximations for the unknown effective electron-electron interaction appearing in this formalism are found to yield accurate results for small atoms and for the uniform electron gas. The basic ideas and open problems of such formalism will be illustrated, and the connection with methods that use a different choice for the model hamiltonian than the non-interacting one of Kohn-Sham will be also discussed.

Border Region Treatment for Fragment-Based Quantum Chemical and Mixed Quantum Mechanical / Molecular Mechanical Approaches

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Accurate descriptions of molecular recognition and chemical reactions are of extreme importance for the understanding of biological processes. On the one hand, quantum chemical calculations are able to lead to such accuracy, but due to the formidable scaling behaviour with system size this can only be done for small molecules using standard methods. On the other hand, molecular mechanics calculations can handle very large biomolecules, but no chemical reaction can be described. To combine the advantages of the two methods *mixed quantum mechanical / molecular mechanical* (QM/MM) calculations have been proposed. In these, only a small part of the system is calculated with an *ab initio* or semi-empirical approach and the rest is treated by means of a molecular force field. A similar idea is followed in fragment-based quantum chemical approaches, in which the molecule is divided into small fragments, which are calculated separately and then recombined to the total molecule. One of the latter methods, the *Field-Adapted Adjustable Density Matrix Assembler* method [1,2], divides a macromolecule, the target, into fuzzy fragments, for which conventional quantum chemical calculations are performed using moderate-size "parent molecules" which contain the fuzzy fragment with some additional local surroundings from the macromolecule. Additional distant parts of the target are represented as point charges in the quantum chemical calculations. Thus, a subdivision into two regions is performed much like in the QM/MM approach and so problems with truncated bonds occur in the same way as in QM/MM. If the region of interest is part of the macromolecule, there are covalent bonds between QM and MM atoms. It is not possible to simply truncate these bonds because this would lead to half-filled orbitals and give an inaccurate description of the electronic state of the QM region. Therefore different methods, like capping hydrogen or pseudo-halogenide atoms, larger capping groups, and localized or hybrid orbitals, were proposed to fill these missing valences. Using the FA-ADMA method, these approximations can be compared directly to the calculation of the total molecule, resulting in quantitative measures for evaluating the accuracies of the used border region treatments [3].

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Theoretical and Computational Approaches to the Chemistry of Alzheimer's Disease

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The central focus of research in our laboratory for a decade or more is the *Radical Model* of Alzheimers Disease (AD). It is an extension of the Amyloid Hypothesis that states that the root cause of AD is the accumulation of the beta amyloid peptide (Aβ), and provides a comprehensive hypothesis of the chemistry that underlies AD. The premise is that the seminal event leading to the death of neuronal cells is damage to neuronal cell membranes caused by free radicals which initiate lipid peroxidation. In the Radical Model, these radicals are long-lived, hydrophobic glycyl radicals or their peroxy derivatives which are carried into the membrane by oligomers of Aβ in β-sheet form. The glycyl radicals are secondary products of methionine oxidation by Aβ-complexed, redox active Cu(II). The structures, stabilities and reactivities of most of the radicals involved in the chain of events that starts with Aβ-bound Cu(II) and terminates in lipid peroxidation are examined in detail by high level computational methods. Special emphasis is placed on the initial step, the oxidation of methionine by the Cu(II)/Aβ complex and the structural and environmental requirements for raising the reduction potential of the Cu(II) and lowering that of the Met sulfide radical cation. Molecular dynamics simulations over timescales approaching a microsecond of free aqueous Aβ and its Cu(II) complexes are examined with a view to finding targets for the design of compounds that prevent the aggregation of Aβ into the toxic oligomeric form.

Role of frontier orbitals in mixed valent trinuclear complex ions

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There are some studies on the mononuclear and mixed valent dinuclear complexes of Fe(II, III) in the literature but we have encountered none on trinuclear complexes. We present the geometrical structures and electronic distribution of the mixed valent trinuclear complexes of $[Fe(CN)_5(\mu\text{-}L)\ Fe(CN)_5\ (\mu\text{-}L)\ Fe(CN)_5]^{n-}$, n = 5,6,7; L= pyrazine, 1,2,4,5-tetrazine. These systems (both cis and trans isomers) have been modeled using B3LYP/631G** with DFT methodolgy. The highlight is on the role and effect of lower lying tetrazine π^* orbitals compared to pyrazine. Metal-ligand charge transfer and intervalence charge tranfer issues are discussed.

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Theory Behind the Charge Distribution on Dissociated Protein Complexes in the Gas Phase

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We will present results from recent calculations that explain aspects of the dissociation of gas phase protein complex ions. It is well known that under certain circumstances this dissociation can produce fragment ions with very asymmetric charge-to-mass ratios. Using a variety of electrostatic and molecular mechanics calculations, we have found that the charge distribution among dissociated fragments could be explained by a Coulomb model based on the repulsion between the net charges on the protein. This model predicts that charges tend to arrange themselves in such a way to maintain approximately a uniform surface charge density, and that the smallest free energy barrier to dissociation should occur when a complex dissociates into two fragments, each carrying the same charge. In particular, it is shown that the charge-to-mass ratio of a fragment ion is not the key physical parameter in predicting dissociation products. In fact, from this perspective, many dissociation pathways reported as "asymmetric" in the literature should be more properly labelled as "symmetric" or "near-symmetric".

Dynamical heterogeneity and violation of the Stokes-Einstein relation in glass-forming liquids

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Over the past decade, identifying and understanding dynamical heterogeneity (DH) in glass forming liquids has added an important new dimension to research on the glass transition. Harrowell and coworkers recently demonstrated (Phys. Rev. Lett. **93**, 135701, 2004), using the concept of "dynamic propensity", that DH is not solely a kinetic phenomenon, and does have an origin in purely configurational properties of the liquid. However, identifying exactly which configurational properties correlate to DH remains an open question. In this study, we broaden the concept of "propensity" to address not only local dynamical properties in a liquid, but also thermodynamic and structural properties. Using molecular dynamics simulations of several model supercooled liquids (one- and two-component Lennard Jones and ST2 water), we show that this approach allows us to identify spatial heterogeneities of local thermodynamic and structural properties that appear on the same time scale as, and that correlate to, the observed dynamical heterogeneities. Our work shows that the growing spatial heterogeneities in a liquid approaching the glass transition are not only dynamical in nature, but can be equivalently discerned as configurational heterogeneities within a generalized propensity analysis. (See Phys. Rev. E **74**, 050502, 2006.)

We will also discuss our recent study of the breakdown of the Stokes-Einstein (SE) and Debye-Stokes-Einstein (DSE) relations for translational and rotational motion in a prototypical model of a network-forming liquid, the ST2 model of water. We find that the emergence of fractional SE and DSE relations at low temperature is ubiquitous in this system, with exponents that vary little over a range of distinct physical regimes. Contrary to previous conjectures, we also show that the same fractional SE relation is obeyed by both mobile and immobile dynamical heterogeneities of the liquid. (See Phys. Rev. Lett. **97**, 055901, 2006.)

Dynamics of organization at the nanometer scale

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Few guidelines exist for designing materials with specific spatial relationships among nanoparticles. In particular, the requirement that target structures be kinetically accessible as well as thermodynamically stable constrains synthetic capabilities in ways that are poorly understood at present. Here I will discuss physical issues associated with this challenge in the context of biomolecular units that access a striking range of collective patterns. Our efforts to model the evolution of such a system over long time scales have revealed some basic, emergent rules of molecular self-assembly, which we expect to apply broadly.

Probing Condensed Phase Electronic Structure and Dynamics with Mixed Quantum-Classical Simulation

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Nearly all practicing chemists now routinely employ mechanical modeling of molecular systems, supplemented by electronic structure calculations, as a means to elucidate or predict likely chemical structures and mechanisms underlying experimental results. However, for electronic processes taking place in a condensed phase, one frequently must account both for elements of the quantum character of the system and a strong coupling between a fluctuating molecular environment and the quantum states of a solute. In this presentation, I will discuss results obtained for two experimentally studied systems using practical theoretical approaches to describe these effects.

The first system to be considered is that of large anionic water clusters. These form a distinctive group of charged species which have been the object of continued controversy for nearly two decades. Starting from just a few molecules, $(H_2O)_n^-$ clusters are found to be stable. The limiting case at large size should be the hydrated electron, a ubiquitous species formed, for example, in the interaction of radiation with liquid water and in numerous photochemical contexts. Hence, the clusters should provide a controlled context for learning about the details of the bulk species. However, experimental efforts have been unable to clearly establish whether the basic structure in such anion clusters is similar to the bulk case, or how large a cluster is required to reach that bulk-like limit. Discussion will focus on a comparative analysis of theory and experiment for electron detachment and optical absorption spectra as a function of cluster size, with the goal of establishing the validity of the clusters as models of bulk solvation. The second example will focus on the dynamics of electron transfer (ET) for a prototypical case of photo-initiated intramolecular ET, in the dye betaine-30 in solution. In particular, we focus on understanding the coupled effects of solvent dynamics, solute structural relaxation, and high frequency intramolecular vibrations on the vibronic dynamics of the ET process using a realistic and detailed description. The contributions to ET rates from such elements will be discussed, along with the realism of models for ET rates that are now used to interpret corresponding experimental data.

Charged solutes in hydrogen bonded systems: Solvation characteristics, dynamics and ultrafast vibrational spectroscopy

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We study the hydration and dynamical characteristics of charged solutes and defects in hydrogen bonded systems by means of a combination of classical and *ab initio* molecular dynamics, population time correlation function and wavelet analysis approaches. Specifically, we have looked at the solvation structure, diffusion, hydrogen bond and residence dynamics and frequency fluctuations in systems containing charged solutes such as halide ions and protonic defects in water in liquid, cluster and supercritical phases. The kinetics of hydrogen bonds that these solutes and defects form with water molecules and their relations to the diffusion and recently reported time dependent vibrational spectroscopic results are investigated [1-3]. We have also studied the localization of an excess electron both in presence and in absence of metal counterions in clusters and fluids consisting of water and ammonia molecules [4]. The power spectra of the hydrogen atoms are calculated for different hydrogen bonding environments and their connections to recent spectroscopic studies are also discussed.

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First Principles Simulations of Nanostructures and Confined Liquids

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Results of *ab-initio* calculations of the structural and electronic properties of nanoparticles and liquid confined at the nanoscale will be presented and compared with experiment. Open issues in modeling materials at the nanoscale by using first principles calculations will be discussed.

Density-functional study of Peierls instability in carbon nanotubes using hybrid functionals

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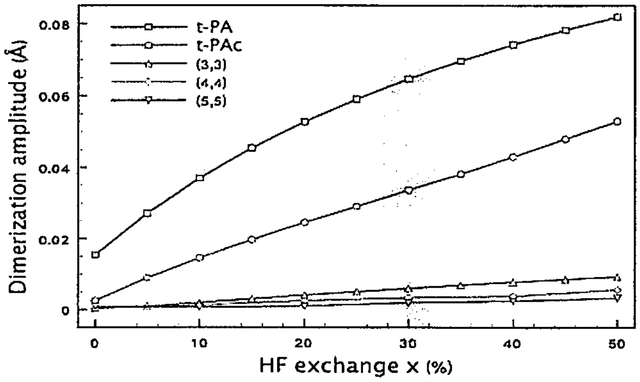
We present a first-principles study of Peierls distortions in *trans*-polyacetylene, polyacene and armchair (n, n) carbon nanotubes. All calculations were done within density-functional theory using a gaussian basis set. We show that while density only functionals (LDA, GGA) cannot reproduce the experimentally measured dimerization in *trans*-polyactetylene, hybrid functionals including Hartree-Fock exchange can give the correct geometry. These findings suggest that armchair (n, n) carbon nanotubes could have a nonsymmetric ground state, in contradiction with what is commonly accepted. Indeed, the B3LYP functional (which includes 20% of exact exchange) opens a gap of 0.26 eV and 0.12 eV for the $(3, 3)$ and $(6, 6)$ carbon nanotubes respectively. Accordingly, dimerization amplitudes of 0.005 Å and 0.002 Å are obtained. It is found that the dimerization and the band gap are proportional to the the amount of exact exchange included in the functional.



How Does Trimethylamine-N-oxide Counter Urea-Induced Protein Denaturation?

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In aqueous solutions trimethylamine-N-oxide (TMAO) acts to counter the protein denaturing effect of urea. Why this is so is a subject of current interest and debate. We have used molecular dynamics simulations to examine this question, and suggest a possible mechanism. Potentials of mean force are obtained for pairs of neopentane molecules immersed in aqueous solutions containing urea, TMAO, or both solutes at once. It is shown that the hydrophobic attraction acting between neopentane pairs in pure water and in water-urea solution is completely destroyed by the addition of TMAO. This implies that TMAO does not counter protein denaturation by enhancing hydrophobic attractions amongst nonpolar groups. Seeking another explanation, we examine the structural and energetic properties of aqueous urea-TMAO solutions. It is observed that TMAO fits very well into the urea-water structure. The TMAO-water and TMAO-urea interaction energies make an important contribution to the total energy of solutions where counter-denaturing effects are observed. TMAO-water and TMAO-urea hydrogen bonds are the the strongest hydrogen bonds in the system. Moreover, TMAO cannot hydrogen bond with itself, and consequently interacts very strongly with both water and urea. Therefore, we suggest that the mechanism of TMAO counter denaturation is simply that water and urea prefer to solvate TMAO rather than the protein, hence inhibiting its unfolding.

Electron correlation through the lens of the Ω intracule

Peter M.W. Gill*, Elise E. Dumont, Deborah L. Crittenden
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Several two-electron distributions can be extracted from a many-electron wavefunction, via the Wigner distribution $W_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2)$. Two of these, the Position and Momentum intracules, are well known and have been discussed by many authors. In recent years, we have introduced six others, the Omega, Wigner, Lambda, Action, Dot and Angle intracules.

The physics of electron correlation depends less on the *absolute* positions and momenta of two electrons than on their relative position $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ and relative momentum $\mathbf{p}_{12} = \mathbf{p}_1 - \mathbf{p}_2$. One also suspects that the absolute directions of the vectors $\mathbf{r}_{12}$ and $\mathbf{p}_{12}$ are less important than their magnitudes r_{12} and p_{12} but that the dynamical angle θ_{12} between them may be significant. It is therefore plausible that most of the important information in $W_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2)$ is captured by the three key variables, r_{12}, p_{12} and θ_{12}, whose joint probability density is

$$\Omega(u, v, \omega) = \int W_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2)\delta(\mathbf{r}_{12} - \mathbf{u})\delta(\mathbf{p}_{12} - \mathbf{v})\delta(\theta_{12} - \omega)\, \mathbf{dr}_1\, \mathbf{dr}_2\, \mathbf{dp}_1\, \mathbf{dp}_2$$

We have called this novel function the Omega intracule.

What use can be made of it? One of the most exciting possibilities is as the foundation of radical new approaches to the electron correlation problem. In standard methods, correlation effects are treated by writing the wavefunction as a lengthy linear combination of determinants. However, this is inefficient and quickly leads to great computational expense. In contrast, a model based on intracules can be physically motivated and much less expensive and we have recently proposed that the correlation energy can be estimated from the Omega intracule through

$$E_c = \int_0^\infty \int_0^\infty \int_0^\pi \Omega(u, v, \omega) G(u, v, \omega)\, d\omega\, dv\, du$$

where $G(u, v, \omega)$ is a universal function that we call the Omega correlation kernel.

In my lecture, I will outline the theory, discuss its computational requirements, and present results for a variety of atomic and molecular systems.

Recent Developments in State-specific Multi-reference Coupled Cluster Theory and Its Approximants

Debashis Mukherjee*
Indian Association for the Cultivation of Science

In this talk, we will present a class of state-specific multi-reference coupled cluster (SS-MRCC) formalisms developed recently, which have proved to be very successful in avoiding intruders via a rigorously size-extensive formulation. All utilize the MRCC ansatz of Jeziorski and Monkhorst but target only the desired state, rather than a group of states as is done in the state-universal (SU-MRCC) formalism. We will discuss two distinct approaches. In the first, the SS-MRCC formalism has more cluster amplitudes than the corresponding number of the virtual functions which form the complement to the model functions in the Hilbert space. This redundancy is exploited to ensure both extensivity and avoidance of intruders. Advantages and limitations of this formalism will be pointed out. In the second approach, which obviates the need of invoking sufficiency conditions to ensure extensivity the SS-MRCC formalism will be shown to be mapped exactly into a dressed CI-like matrix eigenvalue problem which spans just the linearly independent Hilbert space in a given orbital basis. We will explore explicitly how a singles and doubles truncation scheme of cluster amplitudes in this formalism leads to a dressed MR-SDCI which produces manifestly size-extensive and size-consistent eigenvalues. We will also demonstrate how the eigenvalue equation-like structure of the working equations leads naturally to a more robust computational scheme not only for avoiding intruders but also for homing in to a desired eigenvalue. Implications of utilizing just the proper Hilbert space will be discussed, in particular in relation to a linear response version of the formalism for excitation or ionization energies in a strongly quasi-degenerate situation.

Packing and Dynamics in Hard Core Particle Systems.

Richard K. Bowles*
Dept. of Chemistry, University of Saskatchewan

The characterisation and enumeration of jammed packings in hard core particle systems such as hard discs and hard spheres is a long-standing problem. We use some simple hard core particle models to study the relationship between the way particles pack and their dynamics. In particular, a model consisting of hard discs trapped between two walls exhibits the slow relaxation and heterogeneous dynamics characteristic of glassy systems. We are able to exactly enumerate all the particle packings and will discuss the dynamics of the system in terms of two competing theories, the potential energy landscape and dynamical facilitation.

Tracer Diffusion: New Answers to Old Questions

Mark Thachuk*, Gren Patey, Ruslan Sokolovskii, Olga Kravchenko
Department of Chemistry, University of British Columbia

Calculated diffusion constants will be presented for hard sphere tracer particles in a bath of hard spheres as a function of tracer size and bath density. For a range of densities, the behaviour of the tracer diffusion constant can be seen to make a transition from Enskog behaviour (expected for small sizes/low bath gas densities) to hydrodynamic behaviour (expected for large sizes/high bath gas densities). In particular, the slope of the hydrodynamic part matches that derived with slip boundary conditions, as predicted by theory but not confirmed by simulations up to this point. It will also be shown that the diffusion constant of large tracers is very susceptible to finite size effects introduced by the periodic boundary conditions used in the molecular dynamics simulations, and that it is crucial to correct for these effects if accurate results are to be obtained.

Recent simulation results will be shown for rough tracers in a smooth hard sphere bath, as well as rough tracers in a rough hard sphere bath, to relate the behaviour of the hydrodynamic limit to the type of microscopic interactions between the tracer and bath.

Poster Abstracts

Quantum mechanical theoretical analysis of newly-synthesized energetic compounds based on fused-1,2,4-triazine heterocycles

Hakima Abou-Rachid[1]*, Anguang Hu[2], and Louis-Simon Lussier[1]
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We present density-functional theory level predictions and analysis of the basic properties of newly synthesized high-nitrogen compounds, which are based on tricycle fused 1,2,4-triazine and 1,2,4,5-tetrazine heterocycles. Molecular structural properties are clarified, and IR spectra predictions are provided to help detection of those compounds in experiment. The energy content of the molecules in the gas phase is evaluated by calculating standard enthalpies of formation, using a special selection of isodesmic reaction paths. We also include estimates of the condensed phase heats of formation and heats of sublimation in the framework of the Politzer approach. The obtained properties are consistent with those new high-nitrogen compounds being a promising set of advanced energetic materials.

Mechanisms for the Deamination Reaction of Cytosine with H_2O/OH^- and $2H_2O/OH^-$: A Computational Study

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The mechanism for the deamination reaction of cytosine with H_2O/OH^- and $2H_2O/OH^-$ to produce uracil was investigated using ab initio calculations. All optimized geometries were determined at RHF/6-31G(d), MP2/6-31G(d), B3LYP/6-31G(d), and B3LYP/6-31+G(d) levels of theory. Single point energies were also determined at MP2/GTMP2Large and G3MP2 levels of theory. Thermodynamics properties, activation energies, enthalpies and free energies of activation were calculated for each reaction pathway investigated. Intrinsic Reaction Coordinate (IRC) analysis were performed to characterize the transition states on the potential energy surface. Seven pathways for this reaction were found. All pathways produce an initial tetrahedral intermediate followed by several conformational changes. The final intermediate for all pathways dissociate to products via a 1-3 proton shift. The activation energy for the rate-determining step, the formation of the tetrahedral intermediate for pathway D, is 115.3 kJ mol^{-1} at G3MP2 level of theory. This activation energy is in excellent agreement with the experimental value (117 ± 4 kJ mol^{-1}). The results and the mechanisms for these reactions will be presented and discussed.

Quantum Molecular Similarity: an Atoms in Molecules Approach.

H. J. Bohorquez*, R. J . Boyd
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The original quantum similarity method was proposed by Carbo as the integral between the electron densities of the two compared molecules. Besides the relative success of this proposal in quantum QSAR, the equations involved embrace two major drawbacks: a) the similarity results are dependent upon alignment, and b) once provided this mutual alignment, the integral accounting for their similarity degree is expensive in terms of cpu time, mainly because the non-linearity of this integral.

Here we explore Carbo's definition of molecular similarity in order to get an equivalent but simpler procedure to measure it. As a result, we propose an alternative quantum similarity measurement based on the linearity of physical properties as obtained with the quantum theory of atoms in molecules (QTAIM).

We demonstrate that Carbo's proposal can be reformulated in terms of simpler linear expressions. More interestingly, the same equations validate a multipole-based similarity measurement. We illustrate that quantum multipole moments reproduce the electrostatic field symmetries even for atomic systems.

With the proposed methodology it is not only possible to get a perfect alignment between two molecules (or fragments) but also an unbiased similarity measurement in terms of the main electron density symmetries (i.e. multipole moments). We are focused on the theoretical background of QTAIM-based similarity measurement as well on some of its potential applications.

Poster # A-3

Freezing in Gold Nanoparticles.

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Monte Carlo simulation techniques are used to calculate the nucleation free energy barrier for freezing in a 456 atom gold nanoparticle. We find that the solid embryo forms at the surface of the particle and that it is necessary to include the line tension terms, associated with the three-phase contact, in the classical phenomenological model to predict the shape and height of the free energy barrier. Using an alternative free energy order parameter, based on the size of the largest embryo, we observe a limit of stability to the supercooled liquid phase of the cluster at low temperatures. Molecular dynamics calculations of the rate of nucleation supports the idea that freezing becomes a barrierless process at the spinodal.

Poster # A-4

Quadrupole, Octopole and Hexadecapole Moments of Σ, Π, Δ and Φ States. Cylindrically Asymmetric Charge Density Distributions in Linear Molecules with Nonzero Electronic Angular Momentum

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The number of independent components, n, of traceless electric 2^l-multipole moments (Θ, Ω, Φ) is determined for $C_{\infty v}$ molecules in Σ, Π, Δ, Φ states (Λ=0,1,2,3). The value of n can be 1 or 2 depending on both the multipole rank l and quantum number Λ. For $\Sigma^{\pm}$, all 2^l-poles have one independent parameter (n=1). For spatially degenerate states, the general rule is: n=1 for l less than $2|\Lambda|$ but n=2 for higher multipoles with rank $l \geq 2|\Lambda|$. Thus, Π states have *one* dipole (μ_z) but *two* independent multipoles for $l \geq 2$, starting with the quadrupole. Δ states have n=1 for μ, Θ, Ω, but n=2 from the hexadecapole up. What is usually stated in the literature: n=1 *for all possible multipoles of linear molecules*, only applies to Σ states. Our predictions are exemplified by the Θ, Ω, Φ moments calculated for CN, NO, NiH, TiO, CoF, TiF. Π states are most affected by the deviation from axial symmetry; they also obey the (hyper)polarizability inequalitites: $\alpha_{xx} \neq \alpha_{yy} \neq \alpha_{zz}$, and $\beta_{xxz} \neq \beta_{yyz} \neq \beta_{zzz}$. See our JCP (July 2007) paper for details.

PSMC: A novel protein loop modelling algorithm using Preferential Sampling and Monte Carlo refinement

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The elucidation of protein 3D structures has historically been undertaken mainly by experimentalists, in particular crystallographers. However, with advances in computational methods and the availability of a wide range of known protein structures in the Protein Databank, the use of homology modelling as a tool for predicting protein structures has become increasingly popular. Here, we present the development of a novel algorithm for predicting loop regions in protein structures. The newly developed PSMC method uses preferential sampling to bias the search towards more favourable regions of conformational space, using trivariate Gaussian distributions functions to generate appropriate sets of dihedral angles. A Monte Carlo refinement scheme is used to ensure rapid closure of loops, allowing for a large number of loop candidates to be generated quickly. The development and features of the algorithm will be outlined, and validation will be shown for the 4 and 8 residue long loops from the Fiser test set (ftp://salilab.org/andras/loop99/). Various modifications to the algorithm will be discussed and compared for accuracy and efficiency. These include: (1) modifying threshold values in the algorithm, (2) using biased versus unbiased sampling, (3) including cis/trans proline modelling, (4) using confidence intervals to eliminate loop candidates deviating from the ideal trivariate Gaussian distributions, and (5) weeding out loop candidates having steric clashes with the rest of the protein structure.

Are sugars quantum?

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Sugars, apart from being key components of the nucleic acids, play an important role in several biological processes. Thus, several models such as MM3 force field and its earlier variants have been developed and implemented to perform simulation studies on sugars. More recently, a new model, which consists of the conjunction of the AMBER force field and the so-called GLYCAM parameters set, has shown to be reliable for simulation studies of pyranoside systems. A modification to this new force field that incorporates the effect of ring flexibility of furanoside systems has been reported by our group and applied successfully to the methyl α-D-arabinofuranoside. However, there is no report in the literature, to our knowledge, showing quantum simulations in sugars. All studies have been conducted at the classical level. Quantum simulations of molecular systems by means of the Path Integral Molecular Dynamics (PIMD) or Monte Carlo (PIMC) approaches have become very popular in recent years. There are reports in the literature of quantum simulations of water where the importance of quantum fluctuations on various properties has been established. It is reasonable to think that due to the key structural similarities between water and sugars, quantum effects can also be important in the latter. The main motivation of this work is the evaluation of quantum effects on the conformational equilibrium of carbohydrate systems. It has been hypothesized that conformational preferences of sugars along with their interaction with the environment determine their biological activity. In this poster we present a comparative study between classical and quantum simulations carried out on methyl α-D-arabinofuranoside and its dimer, as well as on α-D-arabinopyranoside. Inter-atomic distances, rotamer populations and ring puckering are analyzed and used to showcase the importance of quantum effects. Furthermore, we investigate the free energy profiles (potential of mean force) associated with each distribution.

H-doping effects on surface states of ZnO nanoparticles

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Zinc oxide, a large band gap semiconductor, is known for its gas sensing properties. Its bulk electronic properties are quite sensitive to dopants such as hydrogen, and hence they can be tuned by controlling the doping levels. Furthermore, surface states play a large role in its gas sensing response. In the present report we study H-doping of ZnO with two models: a ZnO cluster of varying size compared with an extended (periodic) ZnO crystal. Quantum chemical calculations, using semi-empirical methods for very large systems and higher level *ab initio* theory for smaller clusters, simulate conditions for a range of doping levels. In addition to relating band gap (or HOMO–LUMO gap) and doping level, we also study the spatial extent of dopant effects on geometry and electronic structure (atomic charge, bond length and strength).

DFT calculations on the electronic structure and geometry of EDTA and its complexes with Mg^{2+}, Ca^{2+}, Sr^{2+}, Na^{+}, K^{+}, and Rb^{+} cations

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Ethylenediamine tetraacetic acid (EDTA) is an amino acid that has been widely used to sequester metal cations. EDTA is used in many industrial plants to complex with heavy metals in order to remove the cations from solutions [1]. It is used as an industrial cleaning agent as well as a detergent to complex with Ca^{2+} and Mg^{2+} in order to reduce the hardness of water [2].
In order to analyze binding properties of EDTA, we decided to compute a binding affinity ladder. Calculations were performed using density functional theory (DFT) using Gill 1996 exchange [3] and Perdew 86 correlation functional [4] (GP86). The following basis sets were used: 6-31G* basis set on carbon, magnesium, calcium, sodium, potassium [5]; 6-31G*+ on oxygen, nitrogen, hydrogen [5]; and a split valence all electron basis set (SVPall) on rubidium and strontium [6]; the SPVall is roughly equivalent to 6-31G* [7]. Computer programs GAMESS [8] and Gaussian 2003 [9] were used to perform the calculations, while Molden [10] was used for visualization.

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First Principle Simulations of Nano-Diamondoids and Semiconducting Single-Walled Carbon Nanotubes

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With the help of recently developed "central insertion scheme" method, hydrogen-terminated diamond clusters (diamondoids) up to 7.3 nm in diameter, single-walled carbon nanotubes (6,5) and (8,3) up to 100 nm in length are investigated at first principle level. We have shown that quantum confinement is still a valid model for diamondoids. It is noted that energy gap continuously decreases with the increase of the size of nanodiamondiods and shows slow convergence. By comparison with experimental X-ray spectroscopies, it is found that except for gap states, overall electronic structures of nano-diamondiods resemble closely with those of bulk diamond. For these nanotubes, the electronic and optical properties become convergence when their lengths increase at 30 nm. The calculated band-gap energies of 100 nm long nanotubes are found to be in good agreement with previous experimental results. Chiral-dependent oscillation behaviors are also discovered for both (6,5) and (8,3) nanotubes. States which arise from the hydrogen-terminated edges are observed for (8,3) nanotube. These states mainly localize around the edges of the tube and locate between the band gap. Although for long nanotubes (>10 nm) these states are quenched and may not be observed in experiments, yet they profoundly affect the electronic and optical properties of short nanotubes (less than 10 nm) and may result in the potential applications in electronic or optical devices.

Ionization of Basic and Aromatic Amino Acids: A Theoretical Study

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Ionization energy, IE, of an amino acid is an important factor, which affects electron-transfer dissociation of $[\mathrm{CuII(ligand)(amino\ acid)}]^{\bullet 2+}$ complexes to yield radical-cationic, RC, form of amino acid in the gas phase. To date, the experimental IE values are known only for a few gaseous basic and aromatic amino acids. In order to predict the IE values, neutral and RC forms of aromatic (phenylalanine, tryptophan and tyrosine) and basic (glutamine, lysine, histidine, asparagine, and arginine) amino acids were studied. The systematic conformational search function of Spartan06 at the HF/3-21G level of theory was used in order to locate low-energy conformers for neutral and RC amino acids. Conformers of lowest energy were then re-calculated using the B3LYP/6-311+G(d,p) method and the MP2(fc)/6-311+G(d,p)//B3LYP/6-311+G(d,p) extrapolation. For each amino acid, adiabatic IE were determined as IE = H0 (RC) - H0 (neutral). The IE values predicted using B3LYP with the 6-311+G(d, p) basis set were in most close agreement with experimental values available. For basic amino acids, ionization of conformers with the COOHN hydrogen bond causes spontaneous proton transfer to the basic side chain and concomitant elimination of carbon dioxide. For aromatic amino acids with the lowest IE, Trp and Tyr, ionization does not significantly affect geometries. The correlation between the IE values and the gaps between the radical-cationic keto-form, $NH_2C(R)HC(O)OH^{\bullet +}$, and the enolic form, $NH_2C(R)C(OH)(OH)^{\bullet +}$, is observed.

Predictions of the Fluorescence Emission Energies of Oxyluciferins: Solvent Effects.

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The CASSSCF and CASPT2 methods have been used to study the structures and electronic spectra of oxyluciferins. Ground and lowest lying singlet excited state geometries of keto and enol forms of the oxyluciferin anion have been optimized at the CASSCF level. CASPT2 has been used to predict relaxed fluorescence energies for the isolated molecules. Planar keto and enol forms are minima on the S0 and S1 potential energy surfaces while the twisted forms are transition states. Research has been extended to examine solvent effects on the fluorescence energies. The CASSCF and CASPT2 models with explicit solvent molecules or in combination with a PCM model of solvation have been used.

Theoretical Studies of the Electronic and Optical Properties of Fluorene-Based Conjugated Copolymers

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Quantum mechanical techniques are applied to investigate the electronic properties of fluorene-based oligomers and copolymers. For the ground states of oligomers, the optimized structures, frontier molecular orbitals, HOMO-LUMO gaps (Δ_{H-L}),in addition to the ionization potentials (IP) and electron affinities (EA) are obtained using the B3LYP/6-31G* density functional theory (DFT) calculations. The lowest excitation energies (E_g) and the maximal absorption wavelength (λ_{abs})of the oligomers are also studied with the use of the time dependent density functional theory (TD-DFT). Next, the linear extrapolation technique is employed to study the polymers' properties. That is, the Δ_{H-L}s, E_gs, IPs and EAs of the copolymers are obtained by plotting the corresponding quantities of the oligomers as a function of the inverse chain length ($1/n$) and extrapolating them to infinite chain length. In addition, the effective conjugation length (ECL) is estimated by the convergence of the excitation energies with the chain length within a threshold of 0.01 eV.

Using complex potentials to calculate electron transmission in molecules.

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The understanding of electron transport through molecular electronic devices (MEDs) is essential in creating new types of circuits that might, one day, be of practical use. We present the formalism behind our newly developed Source-Sink Potential (SSP) method and applications to model systems. Previously, the SSP method has been used to model systems in a tight binding approximation. With it, insight on internal current interference and Fano resonances was obtained. We explored simple relationships between molecular structure and conductance to analyse and predict experiments. The systems studied ranged from small aromatic compounds to nanotubes. Taking advantage of SSP, we described conductance in terms of internal current distributions as well as current carrying wave functions.

Now we outline an implementation of the SSP formalism in the framework of Density Functional Theory (DFT). By creating an interface between an infinite model contact and a realistic DFT molecule, we hope to obtain a quantitative description of molecular conductance

Density functional theory applied to excited states.

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For a variety of molecules, geometries, energies and other properties of excited states calculated by DFT methods are compared with multireference configuration interaction (MRCI) results, as well as with literature values as far as available. In principle, DFT (as well as SCF) methods can be applied not only to the ground state, but also to the lowest state of each irreducible representation of the symmetry group (provided there is any symmetry). So in the case of C2v symmetry, geometries and energies of four states may be obtained for each spin multiplicity. One of these states, usually a singlet, is the ground state. It was found that DFT methods work in general quite well for these low-lying excited states. Provided one uses a high-level basis set, the common dependence of the results on the choice of functional is noted. Second and higher states of a given irreducible representation can also be geometry optimized with DFT methods, as long as their configurations are 'distinct' from those of corresponding lower states; otherwise the wavefunction collapses to a lower state. The quality of such higher-state DFT results needs to be investigated.

Contrary to DFT methods, Time Dependent DFT (TD-DFT) allows for the investigation of excited states beyond the lowest (of each irreducible representation), and is especially useful for obtaining higher vertical excitation energies. Geometries of excited states are much more difficult to obtain with TD-DFT. Since in most applications low-lying states are required, DFT should occupy a top spot in the calculation of their geometry, energy and other properties.

Obviously, DFT methods (as well as SCF) become deficient when ground and/or excited states of the molecule under investigation have multireference character. In an SCF environment, the amount of multireference character depends on the choice of the molecular orbital (MO) set. It is to be investigated to what extent DFT can take care of 'multireference character'.

Poster # A-15

Decoherence and quantum-classical master equation dynamics

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The conditions under which quantum-classical Liouville dynamics may be reduced to a master equation are investigated. Systems that can be partitioned into a quantum-classical subsystem interacting with a classical bath are considered. Starting with an exact non-Markovian equation for the diagonal elements of the density matrix, an evolution equation for the subsystem density matrix is derived. One contribution to this equation contains the bath average of a memory kernel that accounts for all coherences in the system. It is shown to be a rapidly decaying function, motivating a Markovian approximation on this term in the evolution equation. The resulting subsystem density matrix equation is still non-Markovian due to the fact that bath degrees of freedom have been projected out of the dynamics. Provided the computation of non-equilibrium average values or correlation functions is considered, the non-Markovian character of this equation can be removed by lifting the equation into the full phase space of the system. This leads to a trajectory description of the dynamics where each fictitious trajectory accounts for decoherence due to the bath degrees of freedom. Results are illustrated by computations of the rate constant of a model nonadiabatic chemical reaction[1].

In an extension to this problem, the same model is studied using the full quantum equilibrium structure. The quantum calculation provides an enhancement to the rate due to quantum effects such as tunneling. In the framework of the full quantum problem, an alternative approach to calculating the memory kernel is performed in order to provide an analysis of other surface hopping techniques[2].

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Machine-Learning Models in Computer-Aided Discovery of Biodegradable Polymers

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The synthesis of combinatorial polymer libraries for targeted biological screening and applications is a rapidly growing trend in polymer chemistry. Although contemporary assays are highly efficient, it remains impractical to synthesize and evaluate large combinatorial libraries in their entirety. Machine-learning algorithms are invaluable tools in the development of efficient computational models, which could be used to screen virtual combinatorial libraries of biodegradable polymers in silico and to accelerate the discovery process of novel, promising candidates. We present the design of three computational models, which require utilization of the most advanced machine-learning algorithms, namely, Artificial Neural Network (ANN), Polynomial Neural Network (PNN) and Logical Data Analysis (LAD). The ANN model was built to predict fibrinogen adsorption onto the surface of biodegradable polyarylates. This model takes into account more realistic, three-dimensional representation of a polymer derived from MD simulations and therefore, provides significantly better predictions of fibrinogen adsorption in the absence of experimentally obtained data or descriptors. The PNN model was designed to capture both similarity and diversity of polymer structures from the large (up to 40000 compounds) virtual combinatorial library of polymethacrylates and to generate the prediction of cellular response to polymer surfaces. Finally, the LAD model was constructed to identify the most effective gene delivery polymers, to provide their classification and to establish specific correlations between transfection efficiency and polymer chemistry. Theoretical basis, predictive power and advantages of each model will be compared and discussed.

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Influence of molecular geometry and intra-aggregate forces on shapes of self-assembled amphiphilic molecular dumbbells

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Shapes of self-assembled amphiphilic molecular dumbbells have been investigated using a simple geometrical packing equation and Monte Carlo simulations. The molecular dumbbells, when dissolved in a selective solvent, can self-assemble into various shapes of aggregated structures. In order to determine dominant factors that govern the self-assembly of stable and meta-stable structures, we employ a truncated cone shape model of the molecular dumbbell and evaluate critical packing parameters which are essential to geometry dominant self-assembly. For Monte Carlo simulations, various types of intra-aggregate forces are introduced and stable self-assembled structures are sought. Influence of the molecular geometry and the types of intra-aggregate forces on the shapes of self-assembled clusters is discussed.

Amino acid based models for lead-protein binding

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Though it is known that lead replaces calcium in our bones, it is possible that the protein collagen (which is present in bones) may play a role in the binding of lead. Understanding this may allow for better treatment for lead poisoning in the future. Collagen (as with many proteins) is difficult to model because of its large size, so suitable smaller models must be developed. We have developed a model for the various amino acids found in collagen which represents the environment of the amino acid in the full protein, by adding fragments of the polypeptide chain to each amino acid. We find that the lead ions can bridge neighboring amino acids, which could result in different lead adsorption by collagen aggregates than by collagen monomers.

A Comparison of the Performance of the Standard 6-31G and the Binning-Curtiss Basis Sets for 3rd Row Elements

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Most program packages (for example, Gaussian, Gamess etc.) use the Binning-Curtiss (BC)[1] basis set for third row elements. Recently, a standard 6-31G basis set has been developed for G3 calculations[2]. In this study, the performance of these two basis sets is studied by calculating the reaction enthalpies and free energies of some isogyric reactions. The geometries of all the structures were fully optimized at the HF, MP2 and B3LYP levels of theory using the 6-31G(d) and 6-31G(d,p) basis sets. Reaction enthalpies and free energies were also calculated at G3MP2 level, as they are expected to adequately reproduce the experimental data. It is found that the standard 6-31G(d) bromine basis set gives excellent results for all the reactions investigated. However, BC6-31G(d) basis set performs poorly for the reactions which involve 1st, 2nd and 3rd row elements. Since the standard 6-31G(d) basis set performs very well with all the reactions, we recommend that the standard 6-31G(d) bromine basis set be used for calculations involving 3rd row elements.

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Computational Study of a Chloroform-Benzene-Chloroform Complex

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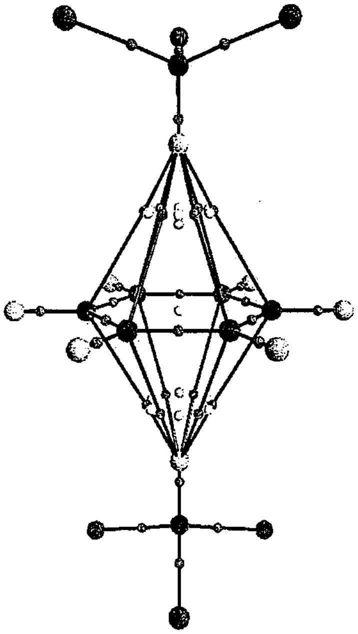
Recently in the literature there has been interest shown in exploring the weak interactions that are known as anti-hydrogen bonds, pseudo-hydrogen bonds or improper, blue-shifting hydrogen bonds. Previously we have examined from a computational perspective 1:1 complexes of trihalomethanes with benzene and substituted benzenes. A 2006 experimental study (Lakshminarayanan, P. S.; Kumar, D. K.; Ghosh, P. J. Am. Chem. Soc., **128**, 9600 (2006)) examined a chloroform-benzene-chloroform (CBC) adduct inside a hexaanthryl octaaminocryptand channel using X-ray crystallography. It was found that the CBC complex has one chloroform molecule on either side of the benzene ring with the CH bond in each pointed toward the plane of the ring and perpendicular to it (see figure 1). In the current study, CBC complex has been examined from a computational perspective. Optimizations, potential energy scans and frequency calculations were performed at the B3LYP/6-311++G(2d,p) and MP2/6-31G(d) levels of theory. In addition, a topological analysis of the electron density of the CBC complex was carried out using the *Atoms in Molecules* theory as implemented in the AIM2000 software. The CH - π interaction will be examined based on the eight criteria for H-bonding proposed by Popelier (*Atoms in Molecules: An Introduction*; Pearson Education Ltd.: Essex, 2000.) Results will be compared to the 1:1 complex previously studied.



QM/MD simulations of Vinca Alkaloid drugs

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Chemotherapeutic drugs that target cellular microtubules are proving to be among the most effective in treating cancer (Jordan and Wilson, Nature Reviews: Cancer, 2004). The Vinca Alkaloids are a class of drugs that target microtubules. In an effort to gain understanding of the mechanism of action of the Vinca Alkaloids and hopefully lead to design of more effective Vinca Alkaloid drugs, QM/MD simulations at the AM1 QM level have been performed on five (5) Vinca Alkaloid drugs that are either in clinical use or in advanced clinical trials. A variety of properties have been calculated including molecular geometries. Of particular interest is the semi-synthetic drug Vinflunine (Hill, Current Pharmaceutical Design, 2001) which adopts a different and unique molecular conformation than the other four drugs in the study, despite similar chemical structures. This conformational difference may account for the different microtubule binding behavior that Vinflunine exhibits when compared to the other Vinca Alkaloids.

Dynamical suppression of decoherence using nonideal laser pulses.

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Maintaining quantum coherence is essential in any quantum information processing scenario, and indeed many techniques have been introduced to combat decoherence. Among these decoupling procedures is Bang-Bang (BB) control, in which the quantum system is exposed to (infinitely) short pulses by an (infinitely) strong laser field. We derive exact equations of motion for a purely dephasing two-level quantum system, embedded in an ohmic environment, driven by nonideal (i.e. finite width, amplitude) BB laser pulses, within the context of quantum-classical Liouville dynamics. A numerical solution is constructed using a hybrid Molecular Dynamics - Monte Carlo scheme, and we compare our results with earlier work on this model, specifically that of Viola and Lloyd (*Phys. Rev. A* 53, 2733, 1998).

Sequence Dependent Coherence Variation in DNA Charge Transfer Processes

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We introduce a numerical scheme based on path integral formalism to measure the coherence length of quantum transport systems. In particular, sequence dependent variation of the coherence length relevant to long-range DNA charge transfer processes is explored and determined by analyzing characteristics of transport pathways. Employing recently developed on-the-fly filtered propagator functional path integral approach, transport pathways with significant contribution can be efficiently sorted, which allows correlation of those pathways to be easily investigated. By performing trajectory space analysis, it was found that the degree of coherence can be characterized by quantifying the correlation of the pair of forward and backward quantum mechanically allowed trajectories. Variation of long-range DNA charge transfer mechanism will also be discussed with respect to bridging sequences.

DFT Study of Band Structure on PA and OLED Materials

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Alternating triphenylamine-fluorene, TPAFn (n=2,3), and tris (4-dihydroxyboranylphenyl) amine (TBPA) copolymers and fluorene-oxadiazole copolymers OxFn (n=2,3) are important components of novel high-efficiency multilayer polymeric blue light-emitting diodes [J. Lu, Y. Jin, J. Ding, Y. Tao and M. Day, J. Mater. Chem., 2006, 16, 593]. In this work we investigate their electronic structure properties using computational approach. Their band structure including band gaps and band widths are studied with the Hartree-Fock (HF) and the density functional theory (DFT) approaches. The polymers are treated as infinite one-dimensional conjugated chains with periodic boundary condition applied to monomeric repeated units. In our study, we consider number of DFT approximations: LSDA, B3LYP, O3LYP, OB95, PBE, PBE1 and TPSS. We employ 6-31G* basis set in all of our calculations and vary number of k-points depending on the size of the system. Comparison of our results with experimental values is made whenever it is possible. For comparison and calibration purposes we also perform calculations for poly(acetylene), PA. The results show that HF method overestimates the band gap of trans-PA by 2.0 eV while the DFT theory underestimates it by 0.23 eV. In all cases of DFT calculations with various functionals, LSDA, B3LYP, O3LYP, OB95, PBE,PBE1 and TPSS, the band gaps are direct and the best agreement with experiment is obtained for the O3LYP functional. The variation of bond length alternation and dipole moments with band gaps will be discussed.

Computational study of the use of naphthalimide derivatives as photosensitizers for selective oxidation of guanine in DNA

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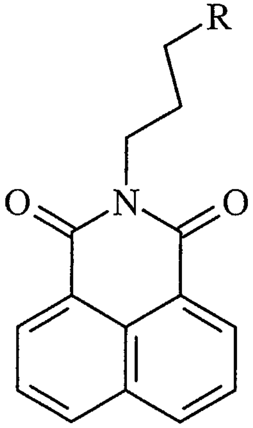
Geometries for five naphthalimide (NI) derivatives have been optimized in the ground state, triplet excited state, reduced and oxidized states using density functional theory (DFT) with the B3LYP hybrid functional and the 6-31G(d,p) basis set. The bond lengths of the NIN derivative showed the most variation from the other four NI derivatives due to the nature of its substituent.

Single point energy calculations, both in vacuum, and solution by including the polarized continuum model (PCM) within the integral equation of formalism (IEF-PCM), at the B3LYP/6-31+G(d,p) and B3LYP/6-311+G(2df,p) levels were performed for each NI derivative. The UV/Vis spectra of the compounds were calculated as well using the time-dependent DFT (TD-DFT) framework, again at the B3LYP/6-31+G(d,p) and B3LYP/6-311+G(2df,p) levels.

The adiabatic and vertical electron affinities and ionization potentials were tabulated for each of the NI derivatives in the ground state, the first triplet excited state and the first singlet excited state. The results suggest that oxidation of DNA by the NI derivatives does not occur via an oxygen dependent type II reaction but may occur via an oxygen dependent type I reaction. This data also suggests that the five NI derivatives studied cannot oxidize any of the DNA nucleobases via direct electron transfer.



DNA-dependent RNA polymerases: Common structures of the active sites and possible reaction mechanisms

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Almost all the known DNA-dependent RNA polymerases (RNAPs) share a universal heptapeptide, called the NADFDGD motif. Based on the available crystal structures of some of these RNAPs, we can see that this motif forms in all cases a loop with an embedded triad of aspartic acid residues. This conserved loop is the key part of the active site. We explore this common active site based on the crystal structures of the yeast RNAP II. To this end, two different modeling methods, the GGA DFT method (PBE) and the reactive force field (ReaxFF), are utilized. The results using the two different methods are compared. In addition, some possible reaction mechanisms are examined with the ReaxFF program.

Carbon-hydrogen bond activation mechanism of aldimine by Rhodium(I) catalyst

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We investigated C-H bond activation mechanism of aldimine by Rh(I) catalyst using ab initio and density functional theory simulations. The C-H bond activation of Rhodium(I)-catalyzed hydroacylation is classified into two mechanisms: direct C-H bond cleavage by the catalyst and electron transfer due to double bond breaking within imine. There are three isomeric structures of $[Rh(PH_3)_2Cl]$ coordinated aldimine, therefore we considered both mechanisms for each structures, respectively. The most probable reaction pathway, which has the lowest activation energy in overall reaction, is explored. It was found that due to the high activation energy of direct C-H bond cleavage by the catalyst, the C-H bond activation of aldimine by Rh(I) catalyst occurs through the electron transfer.

Computation of the Formation Free Energy of Ionic Aqueous Clusters: Equilibrium vs. Non-equilibrium Methods

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In order to gain insight into microsolvation processes, the structure and thermodynamics of ions in aqueous clusters have been the subject of many studies. For instance, the formation free energy of ionic clusters yields significant information that can in turn be compared with available experimental data. While most theoretical estimates of the free energy to date have been obtained by standard equilibrium methods, recent progress in non-equilibrium statistical mechanics has provided a number of powerful (non-equilibrium) techniques for the computation of equilibrium properties.

In this work, we compare the formation free energy of the paradigm $I^-(H_2O)_n$ computed with equilibrium and non-equilibrium techniques. To that effect, we report results calculated with the standard thermodynamic integration method, as well as values obtained with Crooks' fluctuation formalism [G.E. Crooks, J. Stat. Phys. **90**, 1481 (1998)], which relies on the probability of the non-equilibrium work done in the "forward" and "reverse" directions. We compare the relative efficiency and performance of these methods by using classical molecular dynamics simulations with polarizable model potentials. Further, we address the relevance of protonic quantum effects by implementing a straightforward generalization of the thermodynamic integration method in the context of a path integral molecular dynamics (PIMD) algorithm. Finally, we discuss the generalization and possible applications of the non-equilibrium formalism to quantum (path integral) molecular dynamics simulations.

Simulated Electronic Structure Calculation Approach to Molecular Mechanics

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An unconventional approach to molecular mechanics (MM) is presented. Rather than expressing the energy of a molecule as a sum of contributions from stretches, bends, torsions, etc., the total energy is expressed as a sum of electron-electron, nuclear-electron, and nuclear-nuclear potential energies, $E = V_{ee}(R) + V_{Ne}(R) + V_{NN}(R)$, where each energy component depends solely on the *distance* between atoms. The parameters of the electron-electron potential energy function, $V_{ee}(R)$, and the electron-nuclear attraction potential energy function, $V_{Ne}(R)$, can be adjusted to fit total ab initio energies, equilibrium geometries and force constants. Preliminary results will be discussed.

Poster # B-3

New Insights into the Kinetics of the Reaction of Ethene + Bromine -A Computational Study

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The bromination reaction of alkenes is a well known organic reaction. Although the reaction mechanism has been extensively studied experimentally, there have been a limited number of theoretical studies on the bromination of alkenes. Ab initio calculations were carried out for the reactions of Br_2 and $2Br_2$ with ethene. Geometries of the reactants, transition states, intermediates and products were optimized at HF, MP2 and B3LYP levels of theory using the 6-31G(d) and 6-31+G(d) basis sets with both standard and Binning-Curtiss bromine basis sets. Energies were also obtained using G3MP2 and G3MP2B3 levels of theory. Intrinsic reaction coordinate (IRC) calculations were performed to characterize the transition states on the potential energy surface. Comparing the most likely pathway for the reaction with one Br_2 and most likely pathway for the reaction with two Br_2, it is found that bromination should be mediated via $2Br_2$ where the second Br_2 assists in the ionization of the reactant complex to form a bromonium ion/Br_3^- ion pair. There is an excellent agreement between calculated and experimental free energies of activation for the $2Br_2$ reaction with ethene in apolar solvents such as CH_2Cl_2 and CH_2Cl-CH_2Cl. However, in polar solvents such as CH_3OH, the calculated free energy obtained from one Br_2 reaction mediated by a CH_3OH agrees very well with experiment. Finally, a new kinetic expression has been proposed for the bromination reaction of ethene in both polar and apolar solvents.

Poster # B-4

Coherent excitation energy transfer within meso-meso linked Zn(II) porphyrin array with 5,15-bisphenylethynylated porphyrin acceptor

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We investigated coherence length of fast excitation energy transfer processes in donor-acceptor linked porphyrin arrays by means of the on-the-fly filtered propagator functional path integral method. The donor porphyrin array consists of meso-meso directly linked Zn(II) porphyrin units and a 5,15-bisphenylethynylated porphyrin is the acceptor. Based on the simulated dynamics with the optimal potential parameter, details of the EET process are discussed, such as coherence length within the donor arrays. Previously, we have shown that the experimental and the effective two state model system, in which coherence length was implicitly defined, provide excellent agreement. In this work, we used extended multi-state models and determine coherence length from the characteristic off-diagonal trajectory pairs that contribute significantly to the transport dynamics. It was found that the energy bias provided by the acceptor state reduces the system coherence for the short-range transfer and it becomes negligible for arrays with more than 4 donor porphyrin units.

Tracer Diffusion in Rough Sphere Fluids

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In previous work molecular dynamics was empoyed to trace diffusion in hard sphere fluids over a range of density and tracer sizes. In this study, we use conclusions of the previous work to investigate diffusion in another idealized model of the fluid, consisting of perfectly rough spherical molecules that possess convertible energy of rotation. Results are compared with previously calculated diffusion coefficients for smooth spheres.

Poster # B-6

Reduced multireference CCSD and CCSD(T) methods for quasidegenerate states. Theory and some applications

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Single reference coupled cluster methods CCSD and CCSD(T) give a very good description for nondegenerate states, but may fail when describing (quasi)-degenerate systems that arise when handling chemical bond breaking, biradical species, reaction intermediates or multireference (MR) open-shell systems in general.

We focus on recently developed reduced multireference CCSD (RMR CCSD) and its triple-corrected version [RMR CCSD(T)]. For states having a MR character, triples (Ts) and quadruples (Qs) that are singles and doubles relative to the references employed (called primary Ts and Qs) should not be treated perturbatively as in CCSD(T). The RMR CCSD method handles these primary Ts and Qs via the externally-corrected CCSD by relying on the amplitudes provided by a modest-size MR CISD (involving primary Ts and Qs). When the secondary (i.e. non-primary) Ts are subsequently treated perturbatively, we arrive at the RMR CCSD(T).

We present the following applications of the RMR CCSD(T) method:

(i) In contrast to CCSD(T), which incorrectly predicts a singlet ground state for BN, RMR CCSD(T) gives the correct result and an accurate singlet-triplet separation. We also examine quasidegeneracy and symmetry-breaking in the BNB radical.

(ii) Relative to CCSD(T), RMR CCSD(T) gives improved barrier heights for heavy atom transfer, nucleophilic substitution, association, and unimolecular reactions.

(iii) RMR CCSD(T) gives better binding energies and structures for transition metal complexes, such as MCH_2^+, (M=Sc to Cu), and $Ni(CO)_n$.

(iv) When breaking bonds, CCSD(T) PEC often shows an artifactual hump, which is overcome using RMR CCSD(T). Systems examined include main group molecules (e.g., HF, F_2) and transition metal complexes (e.g., $[Sc\cdots CH_2]^+$).

Electric Field Effects on Bipolaron Transport in Polythiophene

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Polythiophene is one of the most widely used materials in the field of semiconducting conjugated polymers. When doped, polythiophene can become a conductor. One of the main goals of studies involving doped conjugated polymers is to identify their charge species and to describe their transport mechanisms. We employ the extended Su-Schrieffer-Heeger's theoretical model (SSH) to study the transport property of bipolaron in polythiophene in the presence of an electric field. This model involves the solution of coupled equations which include the time-dependent Schrödinger equation and the classical motion equation for the lattice displacement which are solved numerically in a self-consistent way. Consistent with other studies, we find that the bipolaron is a preferable charge carrier in polythiophene and, in weak electric field, it moves with little change of its shape along the chain backbone. However, in the presence of a strong electric field, bipolaron tends to spread out as a function of time. This suggests that the strong external electric field (as high as 7.0×10^6 V/cm) decreases the interaction between the lattice and the charge carrier. We also discuss the trend of the energy of the doped polymer with increasing strength of the electric field.

The DFT studies of the formation of C_2 hydrocarbons on the Fe(100) surface

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The Fischer-Tropsch synthesis, which converts the readily available syn-gas ($CO + H_2$) to a large variety of aliphatic and aromatic hydrocarbons, is a process widely employed nowadays in many countries as a means of generating materials of great importance in energy and polymer industries. Despite the long history of application, this process has not yet been fully understood because of the complex reaction mechanisms and strong dependence of product selectivity on the catalysts used in the synthesis.

This presentation will demonstrate the results recenty obtained in our computational investigations utilizing periodic density functional theory on the polymerization reactions of the species relevant to the Fischer-Tropsch synthesis on a single-crystal metal surface. Iron (100) surface was chosen as the catalyst because of its high reactivity in the process. In this work, both the hydrogenation reactions and C-C bond coupling among surface species were studied. Based on the computed thermodynamic and kinetic data, a reaction mechanism accounting for the C-C chain initiation and propagation was proposed which shows a good agreement with the experimental observations.

Fragmentation and Proton Transfer Mechanisms of Radical-Cationic Tryptophan: A Theoretical Study

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The fragmentations of radical-cationic tryptophan, $Trp^{+\bullet}$, which involve the $C\alpha$-$C\beta$ and N-$C\alpha$ bond cleavages, are studied using the B3LYP/6-31+G(d) method. The $C\alpha$-$C\beta$ bond cleavage with elimination of cationic side chain is a low-energy process, which proceeds via a reaction barrier of 11.1 kcal/mol. The rate-determining step on the reaction pathway is a barrier to dissociation of 20.2 kcal/mol. The energies are in accord with experimental observations. Elimination of neutral side chain is a high-energy process. The two possible structures of the neutral fragment, carben, iCHNH, (the $C\beta$ proton transferred to $C\alpha$) and iCH_2N (the NH proton transferred to the carbonyl oxygen), are considered. The carben structure, iCHNH, could not be formed; the extremely reactive carben eliminates a proton from the $Gly^{+\bullet}$ and collapses to the iCH_2NH^+ cation.

The elimination of NH_3 from $Trp^{\bullet+}$ proceeds via the N-$C\alpha$ bond cleavage, which is preceded by the $C\beta$ proton transfer. The following mechanisms for the proton transfer were predicted: (1) the $C\beta$ 1,4 H-shift to the carbonyl oxygen to form $Trp^{+\bullet}$-enolic (barrier of 24.4 kcal/mol), followed by the OH-NH_2 1,4 H-shift; (2) the 1,4 H-shift from the carboxylic group to NH_2 to form $Trp^{+\bullet}$-zwitter-ion followed by the $C\beta$ 1,4 H-shift to the carboxylate oxygen (28.7 kcal/mol); (3) the $C\beta$ 1,3 H-shift to NH_2 (30.7 kcal/mol). The inclusion of entropy factor at 298K changes the order of the limiting barriers in favor of the zwitter-ionic mechanism (2) and makes them competitive (30.1, 31.3, and 31.5 kcal/mol for (2), (1) and (3) respectively).

Poster # B-10

Growth and characterization of Tutton salts

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The cubic mineral Longbenite $K_2Mg_2(SO_4)_3$ and its isomorphs A^{+1} $B^{+2}(SO_4)_3$, where A^{+1} = K, Rb, Cs, TI, NH4 and B^{+2} = Mg, Ca, Zn, Cd, Fe, Co and Ni in the above series of Tutton salts only the ferro electricity of $(NH_4)_2$ Cd_2 $(SO_4)_3$ where reported by Jona & Pepinsky. Attempt was made to understand the speciality of the special application of Zinc ammonium Sulphate and Magnesium ammonium Sulphate mixed crystals. The salts were synthesized and checked for purity by standarad methods of analysis. Large size (9.0) x7.0 x 2.0mm) transparent single crystal of Zinc ammonium Sulphate and Magnesium ammonium Sulphate mixed crystal of various proportions were grown by slow evaporation technique by solution growth method. For the crystallization phenomena Berthelot Nernst, Kholpin and Abu Elameyan equation were tested and the validity of Abu Elameyam suggested the non equilibrium crystallization phenomena. The effect of added impurity and temperature was also studied. The growth kinetics was also investigated.

The crystals grown were characterized for micro hardness and Micro hardness number and yield strength was determined. The crystals were also characterized by XRD, FTIR and thermal studies and the results were discussed. From all these systematic studies, these crystals are found to be laser active at room temperature and above 100 C the crystals are found to be semi conducting and they may be used for temperature dependant switches.

Neural network-based methods for fitting multidimensional potential surfaces and computing wavefunctions

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We propose methods to represent multivariate functions such as molecular potential energy functions or vibrational wavefunctions via lower-dimensional functions which are based on Neural networks (NN). A High Dimensional Model Representation NN (HDMR-NN) is developed to represent potential energy functions as a hierarchy of orders of coupling (a sum of terms each of which depends on a subset of the coordinates). This form facilitates quantum dynamics calculations in which the function is used. The component functions of the HDMR expansion are fitted with NNs. We show that it is possible to lower the dimensionality of component functions of the HDMR by introducing new and redundant coordinates obtained by a linear transformation. The transformation is obtained by a NN, and in the new coordinates, the number of component functions is no longer fixed by the dimensionality of the problem. This allows both to obtain a required fit accuracy with functions of arbitrarily low dimensionality and to allay the problem of a combinatorial growth of the number of component functions in HDMR / multimode type expansions. A combination of an HDMR and NNs in conjunction with redundant coordinates yields a general, molecule-independent method for fitting potentials. We also develop NN-based algorithms to calculate vibrational energies and wavefunctions by combining a NN representation of the wavefunction with methods of linear algebra. The NN representation is equivalent to an expansion over basis functions whose number is moderate as a direct product is avoided.

Poster # B-12

A non-local Wigner-like correlation energy density functional: Parameterization and tests on two-electron systems

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Wigner's correlation-energy density functional utilizes a correlation-energy density of the form $\epsilon_c^W[\rho] = -\alpha/(1 + r_s/\beta)$ where $r_s = [3/(4\pi\rho)]^{\frac{1}{3}}$ is the Wigner radius (of a sphere containing a single particle with homogeneous density ρ), and α and β are parameters. Reparameterization of Wigner's functional yields a good fit to the correlation energies of the helium isoelectronic sequence. However, a quite different reparameterization is required to obtain an equally close fit to the isoelectronic sequence of Hooke's atom.

In an attempt to avoid having to reparameterize the Wigner functional for different choices of the one-body potential, we propose a parameterization that depends on global characteristics of the ground-state electron density as quantified by scale-invariant combinations of expectation values of local one-body operators. This should be viewed as an alternative to the density-gradient paradigm, allowing one to introduce the non-local dependence of the density functional on the density in a possibly more effective way.

Reference parameterizations are obtained using a series of one-body potentials that linearly interpolate between the Coulomb and Hooke cases. Then tests of the reference parameterizations are made for two-electron systems with one-body potentials, $v(r) = \mu\,\mathrm{sgn}(\zeta)\, r^{\zeta}$ with $\zeta = -\frac{1}{2}, +\frac{1}{2}, 1$, which range in a *non-linear* manner between the Coulomb ($\zeta = -1$) and Hooke ($\zeta = 2$) potentials. Encouraging results are obtained.

J. Katriel, M. Bauer, M. Springborg, S. P. McCarthy and A. J. Thakkar, *J. Chem. Phys.* **126**, in press (2007).

Do added water molecules break the strong hydrogen bonds in the formic acid dimer?

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It has been known for more than forty years that formic acid forms a very strong dimer in the gas phase. Numerous studies, both experimental and theoretical, have shown that the resonance-assisted structure of this dimer has two strong, nearly linear, O–H$\cdots$O hydrogen bonds.

If the formic acid dimer is solvated, will the water molecules form a network connected to the dimer or will they disrupt the dimer? If the dimer remains intact, will a hydration shell form and how many water molecules will be needed for this? Will the most stable clusters consist of a water oligomer bound to the formic acid dimer? If the dimer is disrupted, will the formic acid monomers remain connected by one hydrogen bond? Will water oligomers insert themselves between the two formic acid monomers?

Calculations using the B3LYP density functional, 2nd-order Møller-Plesset (MP2) perturbation theory, and good quality basis sets were made on the stepwise micro-solvation of the formic acid dimer to examine these fascinating issues. Fairly extensive potential-energy-surface explorations were made for the $(HCOOH)_2(H_2O)_n$ clusters with $1 \leq n \leq 5$ to ensure that no energetically important minima are missed. Many interesting structures were found. Given the complexity and subtle energetics of the problem, it is not entirely surprising that no simple patterns could be identified.

Ionization of Gaseous Aliphatic Amino Acids: A Theoretical Study

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A systematic conformational search of SPARTAN'06 at the HF/3-21G level of theory was performed to predict low-energy conformers of neutral and radical-cationic gaseous glycine, alanine, cystein, valine, serine, isoleucine, leucine, aspartic acid, threonine, proline, and methionine. The low-energy conformers for each amino acid were selected and optimized using the B3LYP/6-311+G(d,p) method and MP2(fc)/6-311+G(d,p)//B3LYP/6-311+G(d,p) extrapolation. The lowest-energy conformers for the neutral amino acids predicted with this technique are in good accord with the previously reported results on neutral Gly, Ala, Val, Leu, Ile, Pro, Cys, Ser, and Thr. The adiabatic IE for each aliphatic amino acid were calculated as IE = H0 (RC) - H0 (neutral). The IE values predicted using the B3LYP/6-311+G(d,p) method are in good accord with available experimental values while the MP2 method somewhat underestimated the IE values. Ionization causes significant elongation of the Cα-Cβ bond for Cys, Ser, Val, Leu, Ile, Thr, and Asp and the Cα-C(O)OH bond for Ala. The elongated C-C bond has 1e-2c electronic structure, thus, mechanistically, ionization occurs from the C-C bond. For Gly, Pro, Cys, and Met, the geometries around the Cα do not change considerably as ionization occurs from the lone pairs of the N atom of the amino group or from the S atom of the side chain. The correlation between the IE values and the gaps between the radical-cationic keto-form, $NH_2C(R)HC(O)OH^{\bullet+}$, and the enolic form, $NH_2C(R)C(OH)(OH)^{\bullet+}$, is observed.

Experimental and computational NMR studies on the interplay of weak interactions in RNSO·pyridine complexes

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In N-sulfinylamines R-N=S=O the NSO moiety is bent, and in the syn-configured PhNSO this leads to an intramolecular C-HO interaction [1]. The hydrolysis of RNSOs is initiated by another weak interaction, SO, in the pre-reaction complex from the nucleophilic attack of water onto the sulfur atom [2]. We are interested in how far the presence of the C-HO interaction affects the hydrolysis. One approach is to stop the reaction at the complexation stage and use spectroscopic techniques to identify and characterize the weak interactions. Here, we use RNSO·pyridine complexes [3] to keep the interaction to sulfur, SN in this case, but prevent the remainder of the reaction. We will discuss solvent, temperature and concentration dependent ^{1}H and ^{17}O NMR studies of aromatic RNSOs, in conjunction with calculated chemical shifts, to show the presence of both C-HO and SN interactions, and their mutual influence. ^{17}O chemical shifts in aromatic amides and nitro compounds, experimental as well as calculated, will be used for comparison.

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Nucleation of NaCl nano-particles in supercritical water: A Molecular Dynamics study

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The formation of solid NaCl nano-particles from aqueous solutions in the supercritical region is studied using the Molecular Dynamics (MD) simulation method. We have examined the thermodynamic states relevant in the operation of power turbines and supercritical water oxidation reactors. We have chosen to work with 5.1 %wt NaCl solution in the temperature and density range of 673 to 1073 K and 0.17 to 0.34 g/cm^3, respectively. Critical nuclei, cluster lifetimes and size/shape distributions are presented. The size distribution of emerging NaCl clusters shows a very strong dependence on the system density, with larger clusters formed at lower densities. The clusters consisting of approximately 20 ions appear critical for the nucleation dynamics examined. Lifetimes for clusters containing more than 20 ions are found to be on the order of 10 ps and vary with changes in the system density and temperature.

Post Hartree-Fock calculation with one-electron model atom: Application to large transition metal complexes

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Though many theoretical studies of transition metal complexes have been carried out with the DFT method, this method sometimes presents unreasonable results.[1] This means that post Hartree-Fock method is necessary to study the transition metal complexes. We recently reported that the MP2 to MP4 methods present completely wrong energy change in the oxidative addition of H_2 to $Ni(PH_3)_2$ and that the CCSD(T) or CASPT2 method is necessary to present reliable results.[2] However, it is not easy to apply those methods to transition metal complexes. One of the reason is that the size of transition metal complex becomes very large when large substituent is involved in ligand.

We wish to present here the CCSD(T) calculation with one-electron model atom to reproduce the electronic effect of bulky substituent groups such as alkyl groups. In this model, the electronic effect of the substituent is reproduced well by effective potential and the steric effect is taken account of as a steric repulsion correction (SRC). By using this computational method, we calculated the activation barriers and reaction energies of the reductive elimination of ethane from $M(Me)_2(PR_3)_2$ [M = Ni, Pd, Pt, R = H, Me] with CCSD(T), MP4(SDQ), and DFT methods. The $C^{\#}$, which is the model of Me, can reproduce well the results of real Me system, while H cannot. The detailed and other results will be shown in poster session.

Table 1. Activation barrier (E_a) and reaction energy (ΔE) (kcal/mol) of the reductive elimination of ethane from $Pt(Me)_2(PR_3)_2$.

	CCSD(T)		MP4(SDQ)		DFT(B3PW91)	
R	E_a	ΔE	E_a	ΔE	E_a	ΔE
Me	N/A[a]	N/A	53.3	−5.0	51.6	−11.7
H	52.0	−2.0	49.6	−4.9	48.1	−9.0
$C^{\#}$	56.0	−1.2	52.2	−5.6	51.9	−9.6
$C^{\#}$+SRC	56.0	−2.0	52.2	−6.5	51.2	−11.8

a) N/A represents that the results are not available because the system is too large for CCSD(T) calculation.

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(2) Ohnishi, Y.; Nakao, Y.; Sato, H.; Sakaki, S. *J. Phys. Chem. A. in press.*

Competitive Proton-Transfer and Electron-Transfer Dissociations of Ternary Cu(II)-Histidine Complexes.

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The formation of radical-cationic $\text{His}^{\bullet+}$ in the gas phase from the radical-dicationic complexes, $[(\text{L})\text{Cu(II)His}]^{\bullet 2+}$, where L= diethylenetriamine (dien) and 1,4,7-triazacyclononane (9aneN3), is examined using the B3LYP/6-31+G(d) method. For the $[(\text{L})\text{Cu(II)His}]^{\bullet 2+}$ complexes, the lowest-energy structures are zwitter-ionic. The competition between hydrogen-transfer (PT) and electron-transfer (ET) dissociations of the complexes leading to the formation of either HisH^{+} or $\text{His}^{\bullet+}$ depends strongly on the nature of L. The $[\text{CuII(dien)His}]^{\bullet 2+}$ and $[\text{CuII(9aneN3)His}]^{\bullet 2+}$ complexes have different electronic structures of the cupper centers. The electronic structure of the $[\text{CuII(dien)(His)}]^{\bullet 2+}$ complex allows facile, Cu-N or Cu-O coordinated, migrations of the His-fragment toward dien, followed by PT and dissociation. In contrast, for $[\text{CuII(9-aneN3)(His)}]^{\bullet 2+}$, the His-fragment is locked between the two lobes of the dxy-type orbital that prevent migrations towards the 9-aneN3 ligand required for PT dissociation. Thus, the PT dissociation for $[\text{CuII(9-aneN3)(His)}]^{\bullet 2+}$ occurs with a higher activation barrier than the ET dissociation.

The methylation of dien does not block the PT-transfer channel: the methylene hydrogens can be transferred by the migrating His-fragment. Although the limiting reaction barrier to the C-H PT dissociation is notably higher (42.5 kcal/mol) than that to the N-H PT dissociation (28.3 kcal/mol) the ET dissociation of the methylated dien complex is apparently higher in energy.

Insight into the Catalytic Activity of Selenium-Containing Antioxidants

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Selenoenzymes are well known to reduce harmful peroxides in the human body and to protect against oxidative damage, which has been implicated in a variety of disease states including even the process of aging. The significant research effort to understand the chemistry of selenoenzymes, in particular Glutathione Peroxidase (GPx), has led to the development of many small molecule GPx mimics that exhibit similar reductive properties and are, therefore, potential drug candidates. In particular, ebselen (2-phenyl-1,2-benzisoselenazol-3(2H)-one), due to its anti-inflammatory, antiatherosclerotic, and cytoprotective properties in both in vitro and in vivo models, has been studied extensively. In this talk, the results of recent density functional theory investigations of the oxidation of ebselen, ebselen selenol, and ebselen diselenide by hydrogen peroxide[1][2], as well as the effect of electron withdrawing groups and small structure variations on its reductive ability, will be described. Specifically, the topology of the electron density in these systems is studied using the quantum theory of atoms in molecules in order to characterize the complexes and transition states associated with these reactions and to deduce on an atomic scale the origins of catalytic reduction by selenium.[3]

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Role of Polarization in Simulations of Excited-State Dynamics: $NaI(H_2O)_n$ Photodissociation as a Case Study

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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 $NaI(H_2O)_n$ 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 $NaI(H_2O)_n$ relaxation, the results of which can then be compared to and used to interpret experimental results.

Spatial Hydration Structures of Aromatic Molecules in Ambient and Supercritical Water

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The spatial hydration structures of selected aromatic compounds (benzene, phenol and naphthalene) are examined from ambient to supercritical conditions using molecular dynamics (MD) simulations. Detailed 3-D spatial atomic density maps (3-D atomic pair-density distribution functions) of the hydrated water molecules reveal the formation of distinct π-type H-bonded complexes with aromatic molecules at ambient conditions. The effects of the hydrophilic substitution group (phenol) and size of aromatic system (naphthalene) on the hydration structures of aromatics are examined. The number of π-type H-bonds and overall coordination numbers are calculated. Disappearance of the π-type complex of water with aromatic rings is observed near the critical point.

Poster # B-22

Dissociative Electron Attachment to Biomolecules

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We studied dissociative electron attachment (DEA) to adenine and other molecules. The positions of hydrogen detachment due to EA are predicted and we tried to model this process by identifying the relevant MOs and by calculating the dissociative potential energy curves. The work is related to recent experiments showing that electrons with very low energies eV already lead to abstraction of a hydrogen atom. The main results are:

(I) The electron affinities of adenine and related species are all negative, their anions are less stable than the neutral molecule and a distant electron. G2(MP2) calculations show that less than 1 eV is required for abstraction of H from the N9 position of the molecular anion. Like in similar cases, the energy required for the formation of the anions without one H is considerably less than the one needed for bond-breaking in the neutral case.

(II) The neutral and anionic $E=f(r_{N9-H})$ curves are shown in the picture. In the region left of the crossing ($r_{N9-H} < 1.4$) the anion is not stable and its energy must be calculated by special methods. For this, we (a) identify the lowest σ^* - orbital from a Hartree-Fock calculation of the neutral molecule; (b) inspect this MO to see if it exhibits σ^* - character at the N9-H bond and (c) calculated its energy with the OVGF method as a function of r_{N9-H}. Negative EA values are obtained by extrapolation of the positive branch towards smaller distances. The total energy of the anion is derived as sum of the EA plus the energy of the neutral molecule.

(III) The electrostatic potential (ESP) of the molecule influences the shape of the diffuse anionic MO. This can probably explain the different DEA spectra of otherwise similar molecules.

Uranyl Hydroxide

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The early actinide elements in their high oxidation states [An(V), An(VI)] often form stable linear actinyls $[AnO_2]^{n+}$, An = U, Np, Pu and n = 1, 2, that can complex with a variety of ligands in the equatorial plane. Uranyl hydroxide, $[UO_2(OH)_4]^{2-}$, is the prototypical uranyl complex in alkaline solution such as found in waste storage tanks. It has first been isolated and characterized experimentally by Clark and co-workers [*Inorg Chem 1999, 38, 1456*] who found a number of remarkable features. Notable among those are **(i)** a dynamic equilibrium between tetra- and penta-coordination in the equatorial plane, and **(ii)** a facile oxo ligand exchange between axial and equatorial positions [experimental activation energy 9.8 (7) kcal/mol.] The latter observation, in particular, is highly unusual in that it appears to contradict the well-known stability of the uranyl bond, and it has eluded a mechanistic explanation until now.

We have applied relativistic density functional theory (DFT) to the study of uranyl hydroxide and related complexes. Our findings include the following: **(i)** prediction of stable "cis-uranyl" isomers containing a bent uranyl unit; **(ii)** investigation of the equatorial coordination number and the 4/5 equilibrium; **(iii)** proposal of a three-step mechanism for the oxo-ligand exchange process. The theoretical activation energy of 12.5 kcal/mol in solution compares favorably with experiment. The mechanism involves, as a key feature, a stable $[UO_3(OH)_3]^{3-}$ intermediate that facilitates the ligand exchange through proton shuttling. Extensions to Np and Pu are underway.

Implementation of an Extremely Fast and Linear Scaling Xα Algorithm

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Dunlap's analytical Xα algorithm is implemented and tested against a conventional numerical approach that uses a grid to integrate the exchange-correlation contribution to the Kohn-Sham matrix. In our implementation, an overall scaling factor of 1.3 is achieved. This analytical approach is extremely fast and ideally suited for calculations on large molecular systems, and its utility within coupled potential (i.e., QM/QM) calculations on large molecular systems is demonstrated. Appropriate minimal basis sets for this approachs requisite fits of $\rho^{1/3}$ and $\rho^{2/3}$ are constructed so as to have a method that is both fast enough and reliable enough for such applications.

Density functional study of 13-atom clusters of second row transition metals

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We did an unbiased search of low energy structures of 13-atom metal clusters of second row for different spin states by using TSDS(tabu search in descriptors space). In each case, we compared our lowest energy structure with the high symmetry structures and previously reported structures. Our calculations show that only a few elements(Zr, Ru and Cd) adopt the icosahedral structure as global minimum, and there is a rich variety of cluster structure among different elements, for example, clusters of Nb, Mo and Pd have GM that are characterized by a large surface area, and those of elements Tc and Rh resemble fragments of the hcp or fcc crystal structure. For most elements the GM ground state have higher spin multiplicity such as Y_{13}(2S+1=14), Zr_{13}(2S+1=7), Mo_{13}(2S+1=5), Ru_{13}(2S+1=7), Rh_{13}(2S+1=18) and Pd_{13}(2S+1=7).

Global optimization of 13-atom 5d transition metals

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We did structural global optimization for six 5d transition metals(Ta-Pt). Two optimization algorithms, Tabu Search in Descriptor Space(TSDS) and Simulated annealing (SA), were used and their performances were compared. Energy evaluation was done with PBE exchange-correlation functional implemented by VASP. Due to complexity of the multiplicities of transition metals, we did calculations with full relaxation of multiplicity. Amazingly, we found none of them had an icosahedral ground state structure. We compared thoroughly our results with previously reported structures. Calculations show that our results are the best. To rule out the difference could be introduced by choice of functional, we did local optimization for our results and structures reported by other researchers with LDA and PW91. The LDA and PW91 functionals give similar results to PBE and confirm that we found the best structures to date for these clusters.

Poster # B-27

A new insight into using chlorine leaving group and nucleophile carbon kinetic isotope effects to determine substituent effects on the structure of S_N2 transition states

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Chlorine leaving group k^{35}/k^{37}, nucleophile carbon k^{11}/k^{14} and secondary α-deuterium $[(k_H/k_D)_\alpha]$ kinetic isotope effects (KIEs) have been calculated for the S_N2 reactions between para-substituted benzyl chlorides and cyanide ion at 25°C. These KIEs were then compared with the respective experimental KIEs. The experimental secondary α-deuterium KIEs indicate the transition states for these reactions are unsymmetric. The theoretical calculations at the B3LYP/aug-cc-pVDZ level of theory support this conclusion, i.e., they suggest that the transition states for these reactions are unsymmetric with a long NC-C_α and reasonably short C_α-Cl bonds. The calculated chlorine isotope effects suggest that these KIEs can be used to determine the substituent effects on transition state structure with the KIE decreasing when a more electron-withdrawing para-substituent is present. This conclusion is also supported by experiment. The experimental nucleophile carbon k^{11}/k^{14} KIEs for these reactions do not change significantly with substituent and therefore do not appear to be useful for determining how the NC-C_α transition-state bond changes with substituent. The theoretical calculations on the other hand indicate that the NC-C_α bond shortens as a more electron-withdrawing substituent is placed on the benzene ring of the substrate. However, the changes in the NC-C_α transition-state bond with substituent are very small and may not be measurable. Finally, through theoretical approach the implication of using both chlorine leaving group and nucleophile carbon KIEs to determine the substituent effect on transition state structure is discussed.

Environment Dependent Coherence of a Short DNA Charge Transfer System

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We investigate relationship between charge transfer mechanism and quantum coherence within a short DNA sequences in the presence of AT base pair bridges using a real-time quantum dynamics approach. In the on-the-fly filtered propagator functional path integral simulation, by separating paths that belong to different mechanisms and by integrating contributions of correspondingly sorted paths, it was possible to accurately obtain contribution of different transport mechanisms quantitatively. For a 5'-GAGGG-3' DNA sequence, we analyze charge transfer processes quantitatively such that the governing mechanism alters from coherent to incoherent with respect to the friction strength arising from dissipative environments. Based on the forward-backward path deviation analysis, the coherence variation depending on the environment is investigated numerically.

Establishing a link between molecular polarizabilities and molecular conductance

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In molecular electronic devices, coherent electron transport is often the dominant contribution to the molecular conductance. Conductance calculations made with Green's function methods give valuable results but it is difficult to relate the Green's function approach to concepts familiar in chemistry. On the other hand, the Source-Sink Potential (SSP) approach developed in our group allows one to develop simple structure-conductance relationships. As an example, we study the link between the polarizability of a conjugated molecule and its conductance within the Hückel approximation. Using perturbation theory, we derive a simple formula for the transmission probability in terms of molecular polarizabilities.

Temperature dependence of ice growth from computer simulations

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The heterogeneous crystal growth of a solid phase can be considered as the competition of ordering and disordering processes. While the theoretical consideration would predict a maximum of the growth rate at some temperature below the freezing point, experimental studies of water crystal growth rates did not show such a maximum. In the presented work the temperature dependence of ice growth rate and the system size effects were investigated in molecular dynamics simulations using TIP4P-2005 water model in the temperature range of 210–280 K. Three different systems of growing the 0001 (basal) face of hexagonal ice containing 960, 1800 and 2880 water molecules were studied.

The temperature in the systems was controlled by separate Nosé-Hoover chain thermostats for each water molecule. Starting from initial configurations consisting of about 40 % of hexagonal ice, ice growth rates were determined by freezing up to 75 % of the simulation box. The melting rates were also examined.

It was shown that the ice growth rate reaches a maximum at certain undercooling, relative to the melting temperature, in all the system studied. Further lowering the temperature results in the decrease of the growth rate. From analysis of our rate data it was possible to determine the melting temperatures of the water model. For the larger system the melting temperature was found 251.1 K which is in agreement with the previously reported value of 250.5 K. The medium and the smaller systems had higher melting temperatures of 252.2 and 258.2 K, respectively, indicating a definite dependence on the size of the system. The maximum growth rates obtained were 1.9, 1.4 and 1.1 Å /ns at 244.4, 240.2 and 239.9 K (13.8, 12.0 and 11.2 K undercooling) for the small, medium and large systems, respectively.

DFT Study of Polypyrrolic Macrocycles: Analysis of Actinyl-Oxo-to-Transition-Metal Bonding

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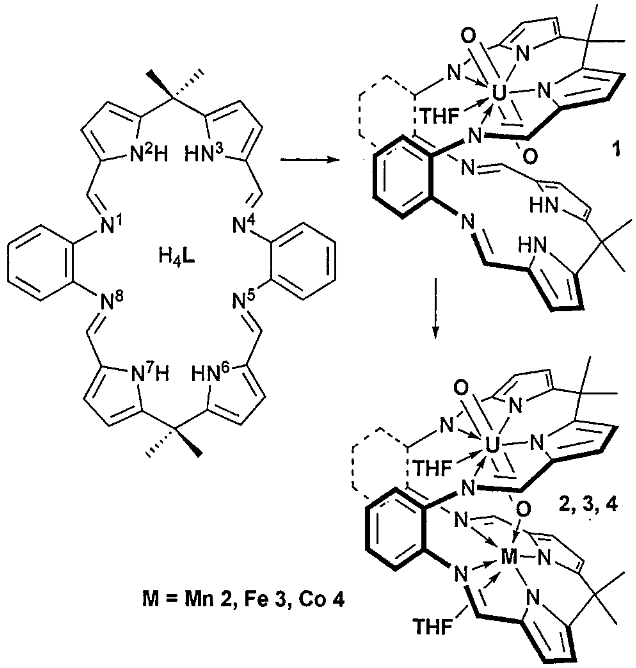
Investigations into polypyrrolic macrocycles continue to produce an abundance of new chemistry. Recently it was shown that the transamination reaction between $\mathbf{H_4L}$ and the uranyl amide $[UO_2(thf)_2(N(SiMe_3)_2)_2]$ in thf at low temperature results in the formation of a tetraanionic hinged polypyrrolic macrocycle **L** which accommodates only one linear uranyl (UO_2^{2+}) **1** within two available cavities, Scheme 1 [*PL Arnold et al., J. Am. Chem. Soc. 2006, 128, 9610.*] Not shown is the hydrogen bonding that occurs between the uranyl-oxo atom and the two imino-pyrrolic H atoms. Further experimental syntheses with $[MN(SiMe_3)_{22}]$ produces **2**, **3** and **4** where M = Mn, Fe and Co, Scheme 1.

In collaboration with the experimental work done at the University of Edinburgh we are performing a computational density functional (DFT) study into related actinyl complexes containing $[AnO_2]^{n+}$ (An = U, Np, Pu, n = 1, 2). Actinyls, in their highly oxidized states, are often found to be very stable. Very few examples of bonding interactions involving uranyl oxygens exist. In particular, the attraction of the 3d transition metals to the internal actinyl oxygen allows us to study the An-O bond in an uncommon extended and weakened state. We have found strong evidence for direct bonds between the transition metal and the actinyl oxygen. Periodic trends along the actinide series as well as along the transition metal series have been investigated.



Molecular Quantum Computing Using The Multi-Configuration Time-Dependent Hartree Approach

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Multi-Configurational-Time-Dependent-Hartree (MCTDH) method for solving the time-dependent Schrödinger equation of the involved states. In particular, three new features have been incorporated in OCT-MCTDH: coordinate dependent dipole moments (useful for any OCT-MCTDH problem), multi-target optimizations (required for quantum computing applications), and simultaneous forward and backward time propagation of the wave function (required for an efficient iterative solution of the OCT equations).

Two simple examples are highlighted to demonstrate the use of OCT-MCTDH: the modified Henon-Heiles potential and a two-dimensional model of acetylene. For both, a controlled transition from the ground state to a vibrational excited state is tested. The acetylene model will be useful in future tests for controlled quantum gate operations using two qubits. Developments toward control of wavefunction phase and new molecular candidates for quantum computing will be presented.

Micro-solvation of glycolic acid: Intramolecular and intermolecular hydrogen bonding

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Glycolic acid, $CH_2OHCOOH$, has rich functionality that allows it to simultaneously form intra- and intermolecular hydrogen bonds, and also allows for weaker C-H$\cdots$O interactions. Raman and infrared spectroscopy studies suggest that glycolic acid exists in a monomeric form in dilute aqueous solution.

A first step towards understanding such a solution is to consider microsolvation in small gas-phase clusters consisting of a glycolic acid molecule (g) and a few water (w) molecules. Will a hydration shell form and how many water molecules will be needed for this to happen? Will the most stable clusters consist of the glycolic acid monomer bound to the surface of a water oligomer? Will the intramolecular hydrogen bond in the acid remain intact? Will the glycolic acid conformation change significantly from its monomeric form?

The lowest-energy structures of gw_{16}, the largest gw_n clusters reported to date [1], consist of a fused, pentagonal-prism $(H_2O)_{16}$ cluster hydrogen-bonded to the carboxylic group of the glycolic acid; the intramolecular hydrogen bond remains intact in the glycolic acid. Low-energy structures with the acid inside a cage-like water cluster were not found.

In this work, we report semiempirical, ab initio and density functional theory calculations on gw_{28} clusters to see what happens when there are significantly more water molecules. To investigate whether clusters with an odd number of water molecules are more or less likely to show a hydration shell, we examine gw_{21} clusters keeping in mind the promising cavity in the w_{21} oligomer.

1. A. K. Roy, J. R. Hart and A. J. Thakkar. Clusters of glycolic acid and 16 water molecules. *Chem. Phys. Lett.*, **434**, 176–181 (2007).

Characterization of Hydrogen Bonding of Water Under Extreme Conditions: Insight From Electronic Structure Calculations

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Despite a wealth of experimental and theoretical studies, the structure of water in the condensed phase is still not completely understood. X-ray absorption spectroscopy provides a sensitive probe of the hydrogen bonding network of a material. This is due to the sensitivity of the probed unoccupied states to changes in hydrogen bonds. In this study, the X-ray absorption spectra (XAS) of several high pressure forms of crystalline and amorphous ices and supercritical water at several densities are investigated. Comparisons to the gas phase and liquid spectra as well as to experiment are made. The changes in the spectral features of the calculated spectra will assist in providing insight into the changes in the hydrogen bonding of water in the condensed phases.

Poster # C-8

Novel Boron-Nitrogen Nano-Needles: Geometry, Electronic Structures and Application of the Nuclear Charge Convexity Theorem

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The theoretical structure of some novel boron-nitrogen nano-needles, (BNNNs), is being presented on this poster. First, the special geometrical features and the energetic stability for the series of $H_3(BN)_{3n}H_3$ $n=1\text{-}10$ is shown. These energetically favored BNNNs were studied based on a quantum mechanical computational method (B3LYP/6-31G(d,p)). Then, an electron density analysis is applied for the calculated molecular orbitals of these nano-needles, using a series of molecular isodensity contours (MIDCOs). Both the bonding regions and the peripheral regions of the nano-needles show characteristic patterns, providing suggestions for additional novel materials. Finally, an energy relation is analyzed for some of these and some additional isoelectronic molecular systems, in particular, the all-carbon nano-needle (ACNN) and BNNN systems, by applying the nuclear charge convexity theorem.[1] Whereas the original relation is valid for identical nuclear geometries with a constant number of nuclei, an extension of the theorem gives additional energy relations for ranges of potential energy surfaces and individually relaxed geometries.

[1] P. G. Mezey, A Simple Relation Between Nuclear Charges and Potential Surfaces, *J. Am.Chem. Soc.* **107**, 3100-3105, (1985)

Adaptive Semi-Empirical Importance Functions for Monte Carlo Simulations

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An adaptive semi-empirical importance function is built in order to better reproduce a DFT potential and improve the sampling in all areas of the potential energy surface during Monte Carlo simulations. The efficiency of the adaptive importance function is demonstrated in a proof of concept application focusing on the reaction of cyclobutene forming butadiene. Compared with a standard AM1 importance function, the adaptive importance function always converges faster, especially near the transition state.

Poster # C-10

Computing Numerical Hessians in Parallel

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When performing a geometry optimization of a given chemical structure, one of the most time consuming tasks is the computation of the Hessian. The process of computing a Hessian can be done both analytically and numerically.

With the influx of large high performance computing facilities (such as ACEnet, WestGrid, HPCVL and SHARCNET) there is even more of an opportunity to take advantage performance gains that can be delivered through parallel computations and algorithms.

This poster presents an algorithm for computing a numerical Hessian and discusses its implementation in combination with the MUNgauss computational chemistry software system.

Test calculations were performed on different structures using different amounts of processing capability. These results are not only compared in terms of performance (timing) but also in terms of accuracy. Observations will also be presented with respect to performance differences between various computer architectures.

Poster # C-11

Geometric and electronic structure of closed-shell bimetallic A_4B_{12} clusters

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We studied a group of 16-atom metallic clusters having general formula A_4B_{12} by density functional theory, where A is divalent and B is monovalent. Global optimization was done in each case followed by calculation of energy second derivatives and vibrational frequencies. The clusters have large HOMO-LUMO gaps ranging 1.2 to 2.6eV and other features suggesting special stability.This is consistent with jellium model and 20 electron count. A T_d symmetry cage structure is found as the putative global minimum for Mg_4Ag_{12}, Mg_4Au_{12}, Cd_4Au_{12} and Ca_4Na_{12}. It is also a low energy isomer for Zn_4Au_{12}, Be_4Au_{12}, Be_4Ag_{12}. The T_d cage structure has ions arranged in shells, with charge +8 and +12, and the importance of symmetry and ion shells is shown by the relative stability of homotops of Mg_4Ag_{12}.

Poster # C-12

Comparison of some multireference perturbation theories at ground and excited states

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Inclusion of electron correlation by second order perturbation theory (PT) starting from the many-electron Fock matrix – the 2nd order Möller-Plesset method – is a well established tool to characterize molecules at their ground state, around equilibrium geometry. Breaking of chemical bonds and description excited states however necessitate a perturbation framework starting from a multideterminantal zero order function. There are several multireference PT (MRPT) formulations that realize this goal. Major differences between the various MRPT theories involve e.g. i) the number of roots which are simultaneously targeted; ii) sensitivity to intruder states; iii) nature of the zeroth order state; iv) whether exactly or approximately size-consistent and extent of possible consistency violation for the approximate variants.

In this study several MRPT methods are compared both in theoretical and numerical terms. Applications focus on second order results. Numerical examples constitute the ground and excited state dissociation curve of the LiH molecule, the classic Be insertion into a H_2 molecule and the twisting of the C_2H_4 molecule. Special attention is payed to realize a fair comparison. This means rigorous application of the same reference function and orbital sets for the different MRPT methods.

A novel group of molecules: hydrogenated and nonhydrogenated BN angular helices. A theoretical study

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Ab initio SCF MO and DFT calculations have been performed on a series of helical structures comprised of boron - nitrogen analogues of N fused benzene rings and alternating N benzene units fused to N-1 cyclobutadiene rings. The electronic structure and stability of BN analogues of angular [N]helicenes (N = 5, 6, 7, 12), [N]phenylenes (N = 7, 13), and their nonhydrogenated versions were investigated at the HF/6-31G(d) and B3LYP/6-31G(d) levels of theory. The presence of an even N number of rings in the boron-nitrogen [N]helicenes leads to the possibility of angular isomers. Electron density contours were calculated in order to interpret the existing bonding patterns. The change in nuclear charges due to the replacement of the C-C with the B-N atompair introduces several specific effects in structure, as well as in the electronic properties, leading to novel molecular systems, such as nanosprings and nanocoils, with potential applications in nanotechnology.

Investigation of Quadruplex DNA Structures Using the Theory of Atoms in Molecules

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The single-stranded overhang of DNA found at the end of chromosomes, known as telomeres, has the ability to form highly ordered quadruplex structures. This is due to the high guanine content and the propensity of guanine molecules to interact with one another to form quartets. Furthermore, these segments of DNA have been implicated to play a role in various disease states. The length of the telomere serves as a checkpoint within the cell lifecycle, signaling cell death once a crisis point has been reached. However, in many tumour cells telomerase, a specialized enzyme capable of extending telomeres, is found to be particularly active, contributing to the immortality of cancer cells. Consequently, telomeres and quadruplex structures have become the focus of intensive research. However, much remains to be understood about these highly ordered structures. The current study investigates these models of quadruplex DNA by use of the theory of atoms in molecules (AIM). Various atomic properties and bonding interactions are compared between the quadruplex structures and the corresponding duplex DNA. In particular, novel binding interactions between the bases themselves or with the sugar-phosphate backbone as well as any energetic differences between the structures are of particular interest. The goal of the study is to determine if any regions of local or global stabilization exist upon the formation of the quadruplex structure. Ultimately it is hoped that this detailed atomic data may indicate how these structures can be stabilized and exploited in therapeutic treatments.

Fluorescent proteins: Benchmarking computational methods against new experimental measurements

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Rational design of color-shifted variants of the *Aquorea* green fluorescent protein (GFP) will require an understanding of the photochemical processes behind the fluorescence characteristics. The interplay of three important factors must be understood: the chromophore, the surrounding protein environment, and the motions of the atoms of both the chromophore and the protein environment. Rather than examining a single fluorescent protein, our work has focused on eleven genetically-engineered mutants of the GFP chromophore that differ in the chemical identity of the substituent R. Computed gas- and solution-phase spectra are compared with newly measured solution phase absorption spectra of the denatured proteins. Several computational methods have been benchmarked against the experimental data set. The results give insight into the reliability of each computational method and an understanding of the role played by the protein environment.

Poster # C-16

Role of frontier orbitals in mixed valent trinuclear complex ions

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There are some studies on the mononuclear and mixed valent dinuclear complexes of Fe(II, III) in the literature but we have encountered none on trinuclear complexes. We present the geometrical structures and electronic distribution of the mixed valent trinuclear complexes of $[\mathrm{Fe(CN)_5(\mu\text{-}L)\ Fe(CN)_5\ (\mu\text{-}L)\ Fe(CN)_5}]^{n-}$, n = 5,6,7; L= pyrazine, 1,2,4,5-tetrazine. These systems (both cis and trans isomers) have been modeled using B3LYP/631G** with DFT methodolgy. The highlight is on the role and effect of lower lying tetrazine π^* orbitals compared to pyrazine. Metal-ligand charge transfer and intervalence charge tranfer issues are discussed.

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Theory Behind the Charge Distribution on Dissociated Protein Complexes in the Gas Phase

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We will present results from recent calculations that explain aspects of the dissociation of gas phase protein complex ions. It is well known that under certain circumstances this dissociation can produce fragment ions with very asymmetric charge-to-mass ratios. Using a variety of electrostatic and molecular mechanics calculations, we have found that the charge distribution among dissociated fragments could be explained by a Coulomb model based on the repulsion between the net charges on the protein. This model predicts that charges tend to arrange themselves in such a way to maintain approximately a uniform surface charge density, and that the smallest free energy barrier to dissociation should occur when a complex dissociates into two fragments, each carrying the same charge. In particular, it is shown that the charge-to-mass ratio of a fragment ion is not the key physical parameter in predicting dissociation products. In fact, from this perspective, many dissociation pathways reported as "asymmetric" in the literature should be more properly labelled as "symmetric" or "near-symmetric".

Poster # C-18

Characterization of Weak Interactions between Aromatic Amino Acids and Natural or Damaged DNA Nucleobases

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DNA damage occurs through a variety of different pathways. For example, alkylation is a very common mechanism, which leads to cationic nucleobases. This damage can be repaired by enzymes (DNA glycosylases) that selectively recognize and remove alkylation damage. Unfortunately, however, the mechanism for this repair is not well understood. Recent crystal structures of DNA glycosylases indicate that modified nucleobases may be held in the active site by aromatic amino acid residues. Our research has been focused on characterizing the gas-phase stacking and T-shaped interactions between aromatic amino acid residues and the natural or damaged nucleobases due to the potential utilization of these interactions by DNA alkylation repair enzymes. The MP2 potential energy surfaces of the nucleobase-amino acid dimers are calculated as a function of several geometrical variables. Our calculations provide fundamental information about the nature of these biologically important weak interactions. Our results also provide computational support for suggestions that alkylation enhances weak nucleobase interactions within the active site of DNA repair enzymes, and provide a measure of the magnitude of this enhancement.

Investigating the Monomer-Dimer Equilibria of Acyclic and Cyclic Stannylene Acetals

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Dialkylstannylene acetals are tin-containing species used extensively as intermediates that facilitate high yield, regioselective, monosubstitution reactions of diols or polyols.[1,2] Because of their favorable properties, dialkylstannylene acetals have become essential synthetic tools in carbohydrate chemistry.[3,4] Although these tin intermediates are widely employed, the exact mechanisms of their regioselectivity reactions are still under debate. Experimental studies have shown that regioselectivity may be caused by the potential aggregation of stannylene acetals monomers into dimers, trimers, and other higher oligomers.[5,6] Although there is an abundance of experimental studies examining dialkylstannylene acetals and their regioselectivity, these tin systems have not been studied extensively by computational methods. Two factors shown to influence oligomeric populations include the nature of acetal substituents (R^1) and the alkyl groups on tin (R^2). Large, bulky, R^1 or R^2 groups may sterically prevent dimer formation.[2] These factors will be investigated in this DFT study using effective core potentials[7] to examine a variety of acyclic and cyclic stannylene acetals. The monomer-dimer equilibrium is explored by examining the geometries, energies, and thermodynamics associated with self-association. This study aims to confirm experimental results as well as shed light on the regioselective mechanisms of dialkylstannylene acetals.

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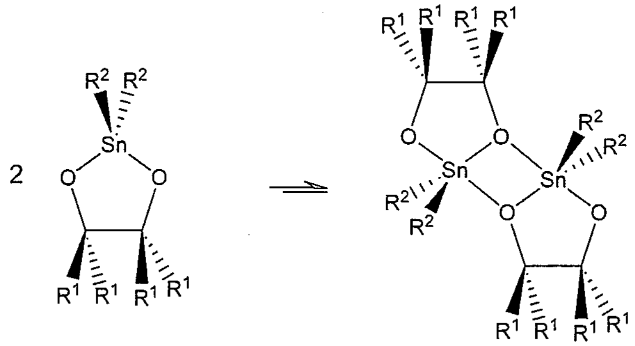

Implementation of *Ab initio* Molecular Dynamics in the Molecular Modelling Toolkit

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Ab initio molecular dynamics involves determining electronic structure "on the fly" rather than utilizing an analytic force field (potential energy surface). While simple molecular dynamics is straightforward, the ability to perform dynamics within existing molecular mechanics software is desirable in order to utilize their many useful features (e.g., integrators, thermostats, analysis tools, etc.). We have successfully implemented the use of an *ab initio* force field in the Molecular Modelling Toolkit (MMTK), a molecular dynamics package, testing the procedure with the molecule CH_3OCl. Currently, the force field is based on MOLPRO, but is readily adaptable to any electronic structure program. Ground state dynamics is performed in order to sample initial conditions for exploring dynamics on the two accessible excited electronic states. Simulations are done with both unconstrained and constrained (C-H bond lengths frozen) dynamics and the results are compared and contrasted. The utility of constrained dynamics, where the number of integration steps can be considerably reduced, is examined.

Poster # C-21

Efficient ab initio Method for Electron Transport and Nonadiabatic Interactions in Molecular Junction/Interfaces

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We have developed new theoretical methods to calculate electron quantum transport across metal-molecule-metal junctions [2-4,6] and photon energy dependence of reaction probability of photodesorption triggered by substrate-mediated excitation [1,5] using nonequilibrium Greenfs function (NEGF) approach. In this talk, we propose an efficient method using an ab initio self-consistent NEGF combined with density functional theory. The resulting algorithm involves three main steps: (i) construction of the embedding potential; (ii) perturbation expansion of the Green's function in the molecular orbital basis; and (iii) truncation of the molecular orbital space by separating it into inactive, active, and virtual spaces. The above procedures directly reduce the matrix size of the Green's function for the self-consistent calculation step, and thus, the algorithm is suitable for application to large molecular systems. Our newly developed method is applied to the Au-benzenedithiol-Au and Au-Au6-Au systems. An importance of the lead structure on the transmission function will be addressed in terms of quantum waveguide effects and an extension of the practical scheme to incorporate electron-phonon interactions will be discussed in order to apply our method to IETS(inelastic tunneling spectroscopy).

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Targeted vibrational excitation of ClO: Optimal control theory and genetic algorithm results

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Controlling chemical processes using shaped laser pulses has been the subject of much theoretical and experimental investigation over the last two decades. However, the realization of a variety of control scenarios has been due to the rapid development of experimental pulse shaping techniques. Optimal control theory (OCT) has been utilized as an effective tool for determining the shaped laser field that will induce a desired quantum process. The optimal control of a laser driven system can be viewed as an inverse problem: rather than knowing the laser field and determining the final molecular states populated after the interaction of the field, a desired final state is "known" and the laser field that takes the system to this state must be found. The goals of optimal control are to achieve a desired quantum process utilizing shaped laser pulses and, importantly, to understand the underlying dynamical processes leading to control.

Results will be presented on using optimal control theory to determine computationally, the tailored laser pulse needed to achieve a desired vibrational excitation in ClO (a nearly harmonic system). Iterative optimization procedures are shown to yield good control (i.e., vibrational population transfer) but produce pulse fields that are very complex. Analysis of the optimized pulses using a cross-correlation frequency resolved optical gating (XFROG) trace suggests the use of simple pulse fields with a small number of adjustable parameters (amplitude, frequency, and chirp). These fields are optimized using the Genetic Algorithm (GA). The control results obtained using the iterative and GA methods are compared and contrasted.

Poster # C-23

The Role of Covalency in AuXe$^+$ system

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The interaction between Au$^+$ and Xe is regarded as the first step to the exploration of interactions between noble metals and rare gases. This interaction has been claimed to be based in either covalency or electrostatics, but despite having been studied for over a decade, its nature still remains disputable[1–4]. Computational studies of AuXe$^+$ system were carried out using the newly developed model core potentials[5,6] and coupled clusters methods[7,8], with extra basis functions optimized to afford superior polarizabilities. Potential energy curve was studied at different levels of theory. Molecular properties such as bond length, infrared frequency, and rotational inertia moment were calculated based on fitting to the potential curve. Wave functions were analyzed by the Natural Bond Orbital method[9,10]. The role of covalency in this interaction was investigated.

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Global optimization of AuN (N=16,32) clusters

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Recently, a lot of effort went into the study of the structures of gold clusters and their anions. There is evidence, from both experiment and theory,that gold clusters possess hollow cage-like structures. Au16 and Au32 appear to have cage structure. In our research, we did global optimization to find the most favored structures for Au16 and Au32, including neutral clusters and anions. We used plane-wave basis sets and PBE exchange-correlation functional implemented by VASP to evaluate energies. Two optimization algorithms were used in our calculations:

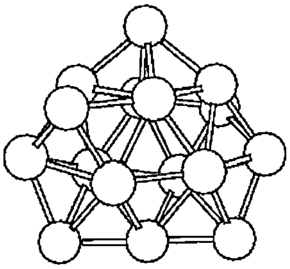
1. Simulated Annealing algorithm supplied by VASP;
2. Tabu Search in Descriptor Space (TSDS) which was developed in our group.

Most important results obtained so far are:

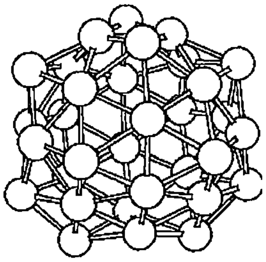
a.the most stable structure for Au16 neutral cluster is flat and has low symmetry, shown in picture below.

b. For both neutral cluster and anion of Au32, the icosahedral cage structure was reported as global minimum. We found a cage structure for Au32 anion which is slightly more stable, shown in picture below.

The low-energy structures we found showed us some very interesting geometries, some cage-like and others compact. We will calculate the photoelectron spectra for the optimized structures and compare them with the experimental results.



Au16



Au32 anion

Poster # C-25

Multi-reference CI studies of photodissociation products of $CHBr_3$: destroying ozone one bromine atom at a time.

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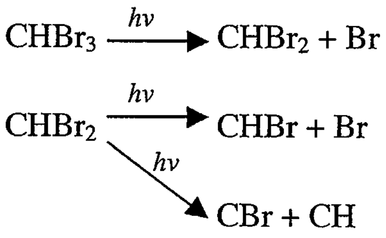
Stratospheric Br and BrO catalytically destroy ozone. One of the arguably dominant natural sources of Br is bromoform, $CHBr_3$, which is produced by ocean algae. This study examines the loss of bromine atoms from bromoform and three of its photodissociation products: CBr, CHBr and $CHBr_2$. The literature gives very little information on the excited states, spectroscopic properties, and dissociation energies of these molecules, making them a perfect group to study both from a fundamental and atmospheric point of view.

The electronic structure and properties were evaluated using the multi-reference configuration interaction method with single and double excitations and corrections for higher excitations, along with a triple-zeta basis set including polarization and Rydberg functions. Twenty different electronic states of CBr were identified, including three excited bound states and several Rydberg states. Similarly, twenty electronic states of CHBr were investigated, yielding excitation and dissociation energies as well as broad geometrical data. Calculations on $CHBr_2$ are ongoing, and are likewise leading to electronic structure determinations.

The atmospheric consequences of these studies will be addressed, and explanations of experimental observations, such as the predissociation of the excited $^2\Delta$ state of CBr, will be given.



$$CHBr_3 \xrightarrow{hv} CHBr_2 + Br$$

$$CHBr_2 \xrightarrow{hv} CHBr + Br$$

$$CHBr_2 \xrightarrow{hv} CBr + CH$$

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