25th Canadian Symposium on Theoretical and Computational Chemistry

CSTCC 25

July 22-27, 2012

University of Guelph

Guelph, Ontario, Canada

Welcome to the 25th Canadian Symposium on Theoretical and Computational Chemistry

CSTCC 25

Welcome to Guelph and the University of Guelph.

CSTCC 25 continues many of the long standing traditions of two series of Canadian theoretical chemistry meetings. The 7th Canadian Computational Chemistry Conference, 7th CCCC, was held most recently at Dalhousie University in Halifax in July 2009. The 17th Canadian Symposium on Theoretical Chemistry, CSTC2010, was held most recently at the University of Alberta in Edmonton in July 2010. The 25 in CSTCC reflects 7 + 17 + 1 and the past and present heritage of this meeting. The CSTCC is intended to cover the full scope of theoretical and computational chemistry, including methodological advances and high level applications.

Our sponsors include:

> The Department of Chemistry of the University of Guelph
>
> Canadian Association of Theoretical Chemists
>
> O'Zone Software

Special appreciation goes to Dr. Uwe Oehler of O'Zone Software who was of immense assistance in handling your abstracts and producing the program book.

We hope that you will enjoy both the social and scientific components of CSTCC 25.

Sincerely, the Organizers,

Prof. John D. Goddard, Department of Chemistry, University of Guelph

Prof. Rene Fournier, Department of Chemistry, York University

Prof. Jeremy Schofield, Department of Chemistry, University of Toronto

Information

Program.

All oral presentations will be held in Rozanski Hall 103 (ROZH 103).

Poster sessions on Tuesday and Thursday will be in the Rozanski Foyer.

Presenters should be at their posters from 14:00 to 15:20 on these days.

The Opening Mixer begins at 18:30 on Sunday July 22 in the Science Complex Atrium

The Registration Desk will be open from 16:00 to 20:00 on
Sunday July 22 in the Science Complex Atrium.

The Registration Desk also will be open 08:30 to 10:30 in the Rozanski Foyer on Monday July 23.

Lunches on Monday and Wednesday will be in Centre 6 on the ground floor of the University Centre.

Lunches on Tuesday and Thursday will be in the Rozanski Foyer along with the Poster Sessions.

The Symposium Banquet is at 18:30 on Thursday July 26 in the Science Complex Atrium.

The Canadian Association of Theoretical Chemists business meeting is in ROZH 103 at 16:40 on Thursday July 26.

Restaurants near the University of Guelph

Fifty West (In the Delta Hotel.)

Montana's Cookhouse 201 Stone Road West

Moonstone 185 Stone Road

Pizza Hut 292 Stone Road West

Moxies Classic Grill 495 Stone Road West (In the Stone Road Mall)

East Side Marios 370 Stone Road West

Swiss Chalet 502 Edinburgh Street

Café Insomnia 649 Scottsdale Drive

Burger King 292 Stone Road West

McDonalds 372 Stone Road West

Kentucky Fried Chicken 620 Scottsdale Drive

Shakespeare Arms 35 Harvard Road

Sunday PM

SC Atrium

Conference Mixer

18:30 Opening Mixer

Monday AM

ROZH 103

CSTCC - Monday

Chair(s) - P.-N. Roy

08:45 Conference Welcome and Introductory Remarks

09:00 0001 *Delocalization and Strong Correlation in Density-Functional Theory* [*][$]**Johnson E. R.** <Chemistry and Chemical Biology, University of California, Merced>

09:40 0002 *A Density-Functional Model for Strong Correlation* **Becke AD** <Department of Chemistry, Dalhousie University, Halifax NS, Canada>

10:20 Coffee Break

11:00 Chair(s) - Viktor Staroverov

11:00 0003 *Pairing Wavefunctions and Universal Functionals for 1-Matrix Functional Theory* [$]**Ayers P.W.** <Department of Chemistry, McMaster University, Hamilton, Ontario>, Johnson P.A., Limacher P.

11:40 0004 *Multireference Equation of Motion Coupled Cluster Theory with applications to Molecular Spectroscopy* **Nooijen M** <University of Waterloo>

12:20 Lunch

Monday PM

ROZH 103

CSTCC - Monday

Chair(s) - Rene Fournier

14:00 0005 *Designing novel clusters using metal atom doping* **Kumar Vijay** <Dr. Vijay Kumar Foundation, 1969 Sector 4, Gurgaon 122001, Haryana, India>

14:40 0006 *Advanced Materials for Clean Energy Applications from Large Scale Virtual Screening and Chemometric Analysis of Metal Organic Frameworks* [*][$]**Woo T** <Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa>, Daff T, Fernandez M, Kadantsev E, Boyd P, Trefiak N

15:20 0007 *Structural dynamics under extreme compression* [$]**Tse JS** <University of Saskatchewan; Department of Physics and Engineering Physics>

16:00 0008 *Theoretical determination of magnetic interactions in ionic solids* [*]**Maurice R.** <University of Groningen, The Netherlands>, Pradipto A. M., Guihéry N., de Graaf C., Broer R.

16:40 End of Session

Tuesday AM

ROZH 103

CSTCC - Tuesday

Chair(s) - Jaime Martell

09:00 0009 *Solvation Structure and Excited-State Dynamics of Ionic Aqueous Clusters* Jahangiri S., Mak C.C., [*][$]**Peslherbe G.H.** <Centre for Research in Molecular Modeling and Department of Chemistry and Biochemistry, Concordia University, Montréal, Québec, Canada, H4B 1R6>

09:40 0010 *Asymmetric top rotors in superfluid para-hydrogen nano-clusters: the molecules with three buckets.* [$]**Zeng T.** <Department of Chemistry, University of Waterloo, Canada>, Li H., [*]Roy P.-N.

10:20 Coffee Break

11:00 Chair(s) - Gabe Hanna

11:00 0011 *Adaptive steered molecular dynamics (ASMD): Unfolding of Neuropeptide Y and decaalanine stretching* [*][$]**Hernandez R** <School of Chemistry & Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400, USA>, Ozer G, Quirk S

11:40 0012 *Interference and Decoherence in Quantum Dynamics: Path Integral Renormalization, Semiclassical and Quantum-Classical Methods* **Makri N** <Departments of Chemistry and Physics, University of Illinois, 601 S. Goodwin Avenue, Urbana, Illinois 61801>

12:20 Lunch

Tuesday PM

ROZH Foyer

Poster Session A

From **14:00** until **15:20**

0013 *Nanoscale Chemically-Driven Dimer* [*]**Colberg P.** <Chemical Physics Theory Group, Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada>, [$]Kapral R.

0014 *In silico construction of Metal Organic Framework materials for high throughput virtual screening and data mining of materials for CO_2 capture.* **Boyd P G** <Center for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, Ottawa, ON>, Daff T, Fernandez M, [*]Woo T K

0015 *Rapid reactivity prediction in direct arylation reactions using machine learning classifiers* **Fernandez M** <Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa>, Gorelsky SI, [$]Woo TK

0016 *An Efficient Method for Transition State Optimization Using Redundant Internal Coordinates* **Rabi S** <Department of Chemistry and Chemical Biology, McMaster University, Hamilton, ON, L8S 4M1>, Verstraelen T, [$]Ayers P.W

0017 *An Exact Density-Potential Relation in Density Functional Theory: A Differential Virial Theorem* [*]**Ryabinkin Ilya G.** <Western University, London, Ontario, N6A 5B7>, [$]Staroverov Viktor N.

0018 *Chemoinformatics based Modelling of Gas Adsorption Properties in Metal Organic Framework Materials* **Fernandez M** <Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa>, Daff TD, Boyd PG, Kadantsev ES, [*][$]Woo TK

0019 *Molecular Dynamics Calculations of Activation Volumes of a Reaction Series: Mechanistic Applications* **Wiebe B.** <Department of Chemistry, University of the Fraser Valley, Abbotsford, BC V2S 7M8, Canada>, Spooner J., Weinberg N.

0020 *Evaporation and Condensation Dynamics in Small Charged Clusters of Water and Methanol* [*]**Daub CD** <Queen's University, Department of Chemistry>, [$]Cann NM

0021 *Binary atomic clusters Sn_mPb_n, $7 \le m+n \le 12$* **Orel V.** <Department of Chemistry, York University, 4700 Keele Street, Toronto, ON, M3J 1P3, Canada>, Fournier R.

0022 *Optimization of van der Waals Parameters for Polarizable Force Fields* [*]**Burger SK** <Department of Chemistry, Wayne State University, 5101 Cass Ave., Detroit, MI 48202>, [$]Cisneros GA

0023 *On the Catalytic Effect of Ethers during Hydroboration of Alkenes* **Sandbeck D.J.** <University of Regina>, [*][$]East A. L. L.

0024 *Silicate Polyol Complexes: A Window on Silicate Biochemistry* [$]**Mawhinney RC** <Department of Chemistry, Lakehead University>, Vis B, Merchant R, Kinrade SD

0025 *Using new quantum chemical methods to investigate NLO properties of linear hydrogen chains* **Limacher P.A.** <Department of Chemistry, McMaster University, Canada>, Wouters S., van Neck D., Ayers P.W.

0026 *The routine construction of vibronic models and their applications to simulation of photoelectron and UV-visible absorption spectra* **Endicott J** <The University of Waterloo >, $^${Nooijen M, Li Y, Goel P

0027 *Stability and Electronic structure of Actinide(IV) Oxide Clusters of Zonohedral Geometry: A Relativistic DFT Study* **Shamov G. A.** <Science, University of Manitoba, Winnipeg MB Canada; IT Division, Kazan National Research University of Technology, Kazan, Russia>

0028 *Concerted and sequential proton transfer mechanisms in water-separated acid-base encounter pairs* Thomas V., Siwick B., [*$]**Iftimie R.** <University of Montreal>

0029 *On the analytical representation of free energy profiles with a the Morse/Long-Range approach: application to the water dimer.* $^${**Tritzant-Martinez Y.** <University of Alberta>, Zeng T., Broom A., Le Roy R.J, [*]Roy P.-N

0030 *Methylarsenic Sorption onto Iron and Aluminum Oxides. A DFT Study.* **Adamescu A.** <Wilfrid Laurier University>, Hamilton I.P., Al-Abadleh H.A.

0031 *Molecular Simulation as a Tool to Aid Interpretation of 67Zn Solid-State NMR for Characterisation of Guest-Host Interactions in Metal Organic Frameworks* **Provost B.R.** <Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, Ottawa, ON, K1N 6N5>, Daff T.D., Sutrisno A., $^${Huang Y., [*]Woo T.K.

0032 *An ab Initio Study of Iron(II) Hydration and Complexation with Chloride* Whynot DCM, [*$]**Pye CC** <Department of Chemistry, Saint Mary's University, Halifax, NS B3H 3C3>

0033 *Chemometric Modeling of Catalyst Enantioselectivity by Molecular Orbital Descriptors* Trefiak NR, **Fernandez M** <Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa>, [*$]Woo TK

0034 *How Glutamine (Trojan horse) Deamidation Reaction induced Hyperammonemia: A Computational Approach* [*]**Halim M. A.** <Department of Chemistry, Memorial University of Newfoundland, St. John's, NL, Canada A1B 3X7; Department of Chemistry & Chemical Biology, McMaster University, Hamilton, ON, Canada L8S 4M1>, $^${Poirier R. A.

0035 *Computational Study of Blue Copper Protein Models* Larade ME, Bierenstiel M, [*$]**Martell JM** <Department of Chemistry, Cape Breton University, Sydney, NS Canada>

0036 *FA^3PS A Code for Fully Automated Adsorption Analysis in Porous Solids for High Throughput Computational Screening* **Daff TD** <Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa>, Boyd PG, Kadantsev ES, Fernandez Llamosa M, [*$]Woo TK

ROZH 103

CSTCC - Tuesday

Chair(s) - Chris Daub

15:20 **0037** *Computational studies of biofluorophores* [*$]**Brown A** <Department of Chemistry, University of Alberta, Edmonton, AB, T6G 2G2>

16:00 **0038** *Molecular shape and compression dynamics of polymer brushes.* [*]**Arteca G.A.** <Département de Chimie et Biochimie, Biomolecular Sciences Programme, Laurentian University, Ramsey Lake Road, Sudbury, Ontario P3E 2C6, Canada, ; Department of Physical and Analytical Chemistry, Uppsala University, , Box 259, S-752 37, Uppsala, Sweden., >, Carlsson T., Kamerlin N., $^${Elvingson C.

16:40 End of Session

Wednesday AM

ROZH 103

CSTCC - Wednesday

Chair(s) - Rob Mawhinney

09:00 **0039** *The Next Generation of High-Quality Benchmarks for Non-Covalent Interactions* [*]**Sherrill C D** <School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400 USA>

09:40 **0040** *Substrate-Assisted Catalysis in Aminoacyl-tRNA synthetases: Insights and New Mechanisms From Computational Chemistry* $^${**Gauld JW** <Dept. Chem. and Biochem., University of Windsor, Windsor, Ontario, N9B 3P4, Canada>

10:20 **Coffee Break**

11:00 Chair(s) - Allan East

11:00 **0041** *A Tail of DNA Damage and Repair* [*$]**Wetmore SD** <Department of Chemistry and Biochemistry, University of Lethbridge, 4401 University Drive West, Lethbridge, Alberta, T1K 3M4 Canada>

11:40 **0042** *Atomic Energies and Richard Bader's Legacy* **Boyd RJ** <Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3>, Albrecht L, Taylor A

12:20 Lunch

Wednesday PM

ROZH 103

CSTCC - Wednesday

Chair(s) - Noham Weinberg

14:00 **0043** *Quantum dots artificial atoms, large molecules or small pieces of bulk? Insights from time-domain ab initio studies* **Prezhdo O. V.** <Department of Chemistry, University of Rochester>

14:40 **0044** *Some challenges in coarse-graining and multiscale modeling of macromolecular systems* $^${**Guenza M.** <University of Oregon, Eugene, OR>

15:20 **0045** *Modeling Electrospray Ionization: From flowing fluid to bare ions* **Cann N.M** <Department of Chemistry, Queen's University, Kingston Ontario>, Daub C., Wu X.

16:00 **0046** *Much ado about icebergs: Hydrophobicity, water and the iceberg model* **Karttunen M** <Department of Chemistry, , University of Waterloo>

ROZH 103

16:40 CATC Business Meeting

17:20 End of Session

Thursday AM

ROZH 103

CSTCC - Thursday

Chair(s) - Tom Daff

09:00 **0047** *An improved method for extending the STO-NG basis sets to all elements of the periodic table* Ferguson JP, [*$]**Pye CC** <Department of Chemistry,, Saint Mary's University, Halifax, NS B3H 3C3>

09:40 **0048** *Dynamics of Conformational Modes in Biopolymers* [*$]**Stepanova M** <National Institute for Nanotechnology NRC; The University of Alberta>, Potapov A

10:20 **Coffee Break**

11:00 Chair(s) - Radu Iftimie

11:00 **0049** *Modeling core/shell and alloy nanoparticles as oxygen reduction catalysts* [*$]**Henkelman GA** <University of Texas at Austin, Department of Chemistry>

11:40 0050 *Quantum non-adiabatic dynamics through conical intersections: Model Hamiltonians and beyond* [*$]**Izmaylov A.F.** <Department of Physical and Environmental Sciences, , University of Toronto Scarborough, Toronto, ON, M1C 1A4; Department of Chemistry,, University of Toronto, Toronto, ON, M5S 3H6>

12:20 Lunch

ROZH Foyer

Poster Session B

From **14:00** until **15:20**

0051 *Mixed quantum-classical Liouville simulation of nonlinear optical response in the mapping basis using the equation-of-motion phase-matching approach* [$]**Hanna G** <Department of Chemistry, University of Alberta>

0052 *A Kohn-Sham-Like Model for the 1-Body Reduced Density Matrix from a Strongly-Correlated Reference* [*]**Johnson P. A.** <Department of Chemistry & Chemical Biology, McMaster University, Hamilton, Ontario, >, Ayers P. W., De Baerdemacker S., Van Neck D., Bultinck P.

0053 *Bimetallic cage clusters.* Afzal S, [*$]**Fournier R** <Department of Chemistry, York University>

0054 *The Oxidative Power of Key Intermediates in the Formation of Ovothiol.* **Bushnell EAC** <Chemistry and Biochemistry, University of Windsor, 273-1 Essex Hall, 401 Sunset Avenue, Windsor, ON>, Fortowsky GB, [$]Gauld JW

0055 *The Origin of the Conductivity Maximum in Molten Salts* **Kuntz C. M.** <University of Regina>, [*$]East A. L. L

0056 *Le-PIGS: a novel method for ground state property prediction* **Constable S.J.** <University of Waterloo, 200 University Ave. W., Waterloo, Ontario, N2L 3G1>, [$]Roy P.-N.

0057 *A Self-Interaction Correction Scheme for Approximate Kohn-Sham Potentials* **Gaiduk Alex P.** <Department of Chemistry, University of Western Ontario, London, Ontario, N6A 5B7, Canada>, [*$]Staroverov Viktor N.

0058 *Pressure-induced phase transitions in crystalline diborane deduced by comparison of simulated and experimental infrared and Raman spectra.* **Torabi A.** <Department of Chemistry, The University of Western Ontario, London, On, N6A 5B7, Canada>, [*]Staroverov V. N.

0059 *Molecular Docking Study of Fk506-binding Protein 35* **MacDonald C** <Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3>, [$]Boyd RJ

0060 *A DFT Assessment of Ovothiol and Ergothioneine Binding to Copper* **De Luna P.** <Department of Chemistry and Biochemistry, University of Windsor, 401 Sunset Ave. Windsor, Ontario N9B 3P4, Canada>, Bushnell E.A.C., [$]Gauld J. W.

0061 *An ab initio investigation of the hydration of the d^0 transition metal tetraoxo complexes* Goodall BL, [*$]**Pye CC** <Department of Chemistry,, Saint Mary's University, Halifax, NS B3H 3C3>

0062 *Metal-free deamination by the Zn(II)-containing metalloenzyme Nicotinamidase? A QM/MM Study.* **Ion B.F.** <Department of Chemistry and Biochemistry, University of Windsor, Windsor, ON N9B 3P4, Canada>, Kazim E., [*$]Gauld J.W.

0063 *A molecular simulation study of water vapour adsorption in metal organic framework materials* **zein aghaji M.** <Centre for Catalysis Research and Innovation,, Department of Chemistry, , university of Ottawa>, Alavi S., [*]Woo T.K.

0064 *Centroid Effective Potential Approach to The Simulation of Large Parahydrogen Clusters and Droplets* **Yang J.** <University of Waterloo>, [*]Ing C., [$]Roy P.N.

0065 *Molecular Dynamics Simulations on Various Weakly Bound Water-Parahydrogen Systems at Low Temperature* **Schmidt M** <Department of Chemistry, University of Waterloo, Waterloo, ON, Canada, N2L 3G1>, Ing C, Constable S, Yang J, Zeng T, Roy P-N

0066 *An Investigation of Metalloporphyrins Containing the First Six 3d-Transition Metals* **Berryman V E J** <Department of Chemistry, Dalhousie University, Halifax, NS, B3H 4J3>, [*]Boyd R J

0067 *Development and Benchmarking of a Density-Functional Approximation for Noncovalent Interactions* [*]**Kannemann Felix O** <Department of Chemistry, Dalhousie University>, [$]Becke Axel D

0068 *Predictions of the Geometries and Fluorescence Emissions of Selenium Oxyluciferins* **Ran XQ** <Department of Chemistry, University of Guelph, Guelph, ON N1G 2W1>, [*]Goddard J

0069 *A DFT Study of the Catalytic Mechanism of Ovothiol A* **Fortowsky GB** <Chemistry and Biochemistry, University of Windsor, 273-1 Essex Hall, 401 Sunset Avenue, Windsor, ON>, Bushnell EAC, [*$]Gauld JW

0070 *Model of Campylobacter jejuni capsular polysaccharide* **Valliani M** <Department of Chemistry, University of Guelph, Guelph, ON>, [*]Boncheff A

0071 *Theoretical study of the structure of silver clusters by Tabu search in descriptor space* [*]**Dhillon Harneet** <Department Of Physics, York university, >, [$]Fournier Rene

0072 *Identification of Transition States Using MD-Generated Volume Profiles and Volumes of Activation* **Wiebe H.** <Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby BC, Canada, V5A 1S6>, Spooner J., Weinberg N.

0073 *Predicting Molecular Properties with Machine Learning* **Heidar Zadeh F.** <Department of Chemistry and Chemical Biology, McMaster University, Hamilton, ON, L8S 4M1>, [*]Ayers P. W.

0074 *Simulation Studies of the Vibrational Dynamics of para-Hydrogen Clusters* **Faruk N. F.** <Department of Chemistry, University of Waterloo>, Li H., Yang J., Le Roy R. J., [$]Roy P.-N.

0075 *Mechanochemistry of Bimolecular Reactions: Quantum Chemical Simulations of 1,3-Dipolar Cycloadditions to Carbon-Carbon Double Bonds* **Carver B. S.** <Queen's University>, [$]Mosey N. J.

0076 *Potential Energy Surfaces of Reaction Systems at Extreme Pressures* **Yanciw B** <Department of Chemistry, University of the Fraser Valley, Abbotsford, BC, V2S 7M8, Canada>, Spooner J, Weinberg N

0077 *Temporal quantum mechanics / molecular mechanics method for extending the time scales accessible in molecular dynamics simulations of reactions* **Dayal P** <Queen's University, Kingston, Canada>, [*$]Mosey N

ROZH 103

CSTCC - Thursday

Chair(s) - TBA

15:20 0078 *Interpreting Barium Blockade Kinetics of Potassium Channels using Multi-Ion Potential of Mean Force Calculations* **Rowley CN** <Department of Chemistry, Memorial University, St. John's, NL>, Roux B

16:00 0079 *Electron transfer and other reactions in proteins:towards an understanding of the effects of quantum decoherence* **Salahub DR** <IBI - Institute for Biocomplexity and Informatics and Department of Chemistry, University of Calgary>

16:40 End of Session

SC Atrium

18:30 Banquet

Friday AM

ROZH 103

CSTCC - Friday

Chair(s) - John Goddard

09:00 0080 *GKCI Approach to Solving the Electronic Schrödinger Equation*
[*$]**Anderson JSM** <Department of Physics, The University of Tokyo, Bunkyo-ku, Tokyo, Japan>, Ayers PW

09:40 0081 *Symmetric two-point weighted density approximation for exchange-correlation energies* **Cuevas-Saavedra R** <Duke University>, Ayers P

10:20 0082 *Water and Aqueous Solutions: New Insights from Large-Scale Computer Simulations* [$]**Patey G.N.** <Department of Chemistry, University of British Columbia>, Overduin S.D., Gupta R.

11:00 Coffee Break

11:40 End of Session

Delocalization and Strong Correlation in Density-Functional Theory

E. R. Johnson[*$] <*ejohnson29@ucmerced.edu*>, Chemistry and Chemical Biology, University of California, Merced.

Accurate treatment of both delocalized and strongly-correlated electrons remains an outstanding challenge for density-functional theory. Most functionals overestimate the energy lowering due to delocalized electrons, as in stretched odd-electron bonds, highly-conjugated systems, and charge-transfer complexes. Functionals simultaneously underestimate the energy lowering arising from non-dynamical electron correlation, as in stretched even-electron bonds, open-shell singlet states, and many transition-metal complexes. We develop a new density-functional approach based on real-space modeling of the exchange-correlation hole. Our starting point is the Becke-Roussel exchange functional, modified to allow flexible hole normalization and with additional non-dynamical correlation terms. Preliminary results demonstrate that the functional is capable of predicting correct dissociation limits for H_2^+, He_2^+, and H_2.
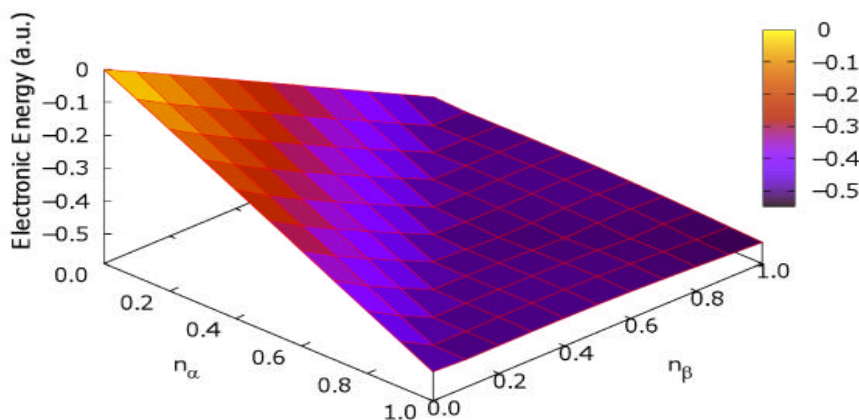
A Density-Functional Model for Strong Correlation

AD Becke <*axel.becke@dal.ca*>, Department of Chemistry, Dalhousie University, Halifax NS, Canada.

By "strong" correlation we mean: the ability to stretch chemical systems, even to dissociation limits, and obtain accurate total energies without breaking spatial and/or spin symmetries. This is challenging for both wave-function and density-functional methods. We will discuss a density-functional model of strong correlation that produces very encouraging results. It is a simple generalization of the "B05" static correlation model of Becke, J. Chem. Phys. 122, 064101 (2005).

Pairing Wavefunctions and Universal Functionals for 1-Matrix Functional Theory

P.W. Ayers[*$] <*ayers@mcmaster.ca*>, **P.A. Johnson** and **P. Limacher**, Department of Chemistry, McMaster University, Hamilton, Ontario.

In Kohn-Sham density functional theory, a reference system of noninteracting electrons with the same density as the physical system is used as a zeroth-order approximation to the system. Using an adiabatic connection to the target system, one can then correct the Kohn-Sham approximation. In this talk, I will establish an analogous approach for the 1-electron reduced density matrix (DM1). The reference system now contains interacting electrons, which we choose to describe with the Richardson Hamiltonian. The reference-state wavefunction includes the noninteracting-electrons limit (Kohn-Sham), strictly-correlated-electrons limit (antisymmetrized geminal power), and strongly orthogonal geminal product (generalized valence-bond like) forms as special cases. Any singlet-state DM1 can be reproduced by a Richardson Hamiltonian, and an adiabatic connection from the Richardson Hamiltonian to the target physical system provides a rigorous definition for the correlation functional in 1-density matrix functional theory (DM1FT). Preliminary numerical results are favorable. If, furthermore, one discards the link to DM1-theory and regards the Richardson wavefunction form as being merely a wavefunction ansatz for conventional quantum chemsitry, strong static correlation can be described at (nearly) mean-field cost.

Multireference Equation of Motion Coupled Cluster Theory with applications to Molecular Spectroscopy

M Nooijen <*nooijen@uwaterloo.ca*>, University of Waterloo.

To treat complicated open shell molecules, e.g. an anti-ferromagnetically coupled bimetal complex, we use multireference coupled cluster methods. I will speak in particular about our latest development, the MR-EOMCC method, which generalizes single reference equation of-motion coupled cluster (EOMCC) to the multiconfigurational case. This method allows the calculation of many electronic states, while using a single set of amplitudes to describe dynamical correlation. The method allows for the construction of vibronic models that describe a limited number of diabatic electronic states, parameterized by a compact set of parameters. In the final step we solve for the (non-adiabatic) nuclear dynamics problem to simulate all features of the spectroscopy.

Designing novel clusters using metal atom doping

Vijay Kumar <*kumar@vkf.in*>, Dr. Vijay Kumar Foundation, 1969 Sector 4, Gurgaon 122001, Haryana, India.

Doping of clusters by a metal atom could lead to novel atomic structures as well as new properties and applications. We predicted [1] novel fullerene-like $Zr@Si_{16}$ and a Frank-Kasper $Ti@Si_{16}$ cluster by doping of a transition metal atom in Si clusters. These predictions have been realized in laboratory. Studies on doping of Si, Ge, Sn, Pb, and even metal clusters such as Au have shown size selectivity and enhanced stability by doping. I will discuss our recent work [2] on metal doped silicon clusters where we have studied the growth behavior by comparing calculated electronic spectra with photoemission results. Our results show novel growth behavior of these clusters. Further doping of Mn in II-VI compound semiconductor clusters has been shown [3] to lead to magic non-stoichiometric clusters. On the other hand doping of rare earths is easier to achieve in nanoparticles [4]. Also Gd doping in Au clusters has been used to make multifunctional magnetic gold clusters and magnetic superatoms [5] that have potential for applications in imaging and cancer therapy.

[1] V. Kumar and Y. Kawazoe, Phys. Rev. Lett. **87**, 045503 (2001); V. Kumar, Comp. Mater. Sci. **36**, 1 (2006), Nanosilicon, Ed. V. Kumar, Elsevier (2008).
[2] S. Jaiswal, V. Babar, and V. Kumar, to be published; V. Babar and V. Kumar, to be published.
[3] S.P. Nanavati et al., Phys. Rev. B**84**, 045306 (2011) and to be published.
[4] P. Kaur et al., Phys. Rev. B **85**, 085429 (2012) and to be published.
[5] B.D. Yadav and V. Kumar, APL **97**, 133701 (2010); P.P. Shinde et al., J. Mater. Sci. in press.

Advanced Materials for Clean Energy Applications from Large Scale Virtual Screening and Chemometric Analysis of Metal Organic Frameworks

T Woo[*$] <*twoo@uottawa.ca*>, **T Daff** <*tdaff@uottawa.ca*>, **M Fernandez** <*michael.llamosa@gmail.com*>, **E Kandantsev** <*ekadants@uottawa.ca*>, **P Boyd** <*pboyd085@uottawa.ca*> and **N Trefiak** <*ntrefiak@uottawa.ca*>, Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa.

Since electricity generation from coal combustion accounts for 40% of our CO_2 emissions worldwide, there is intense interest in CO_2 capture and storage (CCS) because it represents a practical strategy to reduce greenhouse gas emissions in the near term. CCS involves scrubbing CO_2 from the combustion flue gas and permanently storing it. Large scale CCS is presently not a reality because current CO_2 scrubbing technologies are too energy intensive resulting in prohibitive costs. Metal organic frameworks (MOFs) have attracted significant attention as solid sorbants for cost-effective CO_2 scrubbing since they can possess world record surface areas and can show high capacity for CO_2 adsorption. In this presentation, our group's efforts to virtually screen hundreds of thousands of MOFs for gas separation applications related to clean energy will be given. Several promising synthetic targets have been identified from this screening that can realistically be synthesized. In addition to simply identifying synthetic targets from this large scale screening, we are also developing effective chemometric tools to analyze the enormous data sets that are generated. Our new Quantitative-Structure-Property Relationship (QSPR) models and similar chemometric tools to mine relevant knowledge from the large data sets that can be used to guide the development of new materials will be presented.
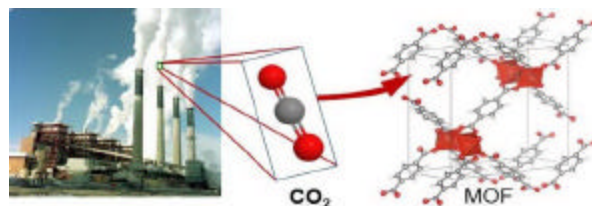
Structural dynamics under extreme compression

JS Tse[*$,] <*John,Tse@usask.ca*>, University of Saskatchewan, Department of Physics and Engineering Physics.

Pressure is a versatile thermodynamic parameter to control the nature of chemical bonding in solids. In recent years, it has been shown that when a material is compressed under high pressure, successive structural transformations will eventually lead to a metal <-> insulator transition regardless of the electronic structure of the initial structure. This has resulted in many novel properties, such as superconductivity. Recent investigations however, have shown that even at low and moderate pressure the nature of chemical bonding can be affected. Interestingly, the modification of the electronic structure through orbital rehybridization can lead to new types of chemical interactions. In some cases, even under compression, the atomic motions can be fluxional. To illustrate this interesting phenomenon, results on recent studies on the structure and dynamics of elemental Ca,H2 solvatedSiH4 and solid hydrogen close to metallization will be presented and discussed.

Theoretical determination of magnetic interactions in ionic solids

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Multiferroic materials are ionic solids presenting simultaneously long-range magnetic orders, ferroelectricity and/or ferroelasticity. In order to be expressed in a manageable set of effective parameters, the magnetic properties of such systems can be described using model Hamiltonians. Such Hamiltonians act on a (small) model space while accounting effectively for all the important interactions of the many-electron Hamiltonian. The extracted parameters can be uniquely translated into the parameters that are commonly used to interpret experimental findings. The accurate determination of such effective interactions in ionic solids is particularly challenging since it requires an accurate treatment of the long-range interactions present in the crystal, of the electron correlation and even of relativistic effects such as spin-orbit coupling. Since in ionic solids the delocalization effects are only moderately important, accurate determinations of local properties such as magnetism can be performed within the so-called embedded cluster approach. Provided that the embedding is well chosen and built, the magnetic interactions can be adequately determined using molecular quantum chemistry methods applied onto a small region of the crystal, the cluster. In this presentation, this approach will be illustrated with the CuO and $LiCu_2O_2$ materials [1,2].

[1] A. M. Pradipto, R. Maurice, N. Guihéry, R. Broer and C. de Graaf, Phys. Rev. B 85 (2012) 014409.
[2] R. Maurice, A. M. Pradipto, C. de Graaf and R. Broer, Phys. Rev. B (accepted).

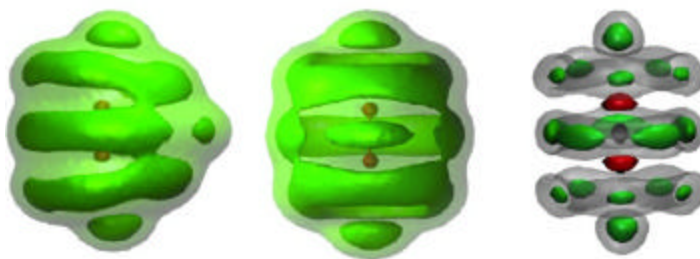## Solvation Structure and Excited-State Dynamics of Ionic Aqueous Clusters

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Ionic aqueous clusters constitute a paradigm for detailed investigations of the ion-water and water-water interactions involved in numerous important biological and chemical processes. In this contribution, we explore and discuss the solvation structure of a variety of ions in clusters and their effect on water structure. In particular, some ions have a higher affinity for the cluster surface rather than the interior as they are unable to affect the water structure significantly. Accordingly, an array of efficient first-principles methods has been developed to simulate quantitatively the solvation structure of ionic aqueous clusters and address this issue. Furthermore, an interesting feature of surface-solvation ionic cluster structures lies in the large dipole moment of the water network and its ability to bind an electron upon photo-excitation. Photo-excited iodide-water clusters, for instance, have attracted considerable interest, since investigation of these clusters may provide new insights into the mechanism of formation of the closely related hydrated electron, one of the simplest yet most mysterious ions of chemistry. Ab initio molecular dynamics simulations of the excited-state dynamics of iodide-water clusters are thus presented; the use of these simulation results along with experimental photoelectron spectra to understand the precise mechanism of excitation and relaxation is then discussed. The cluster structure and dynamics may be understood in terms of the subtle interplay between water-water and ion-water interactions in the clusters.

Asymmetric top rotors in superfluid *para*-hydrogen nano-clusters: the molecules with three buckets.

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We present the first simulation study of bosonic clusters doped with an asymmetric top molecule. A variation of the path-integral Monte Carlo method is developed to study a para-water (pH_2O) impurity in para-hydrogen (pH_2) clusters. The growth pattern of the doped clusters is similar in nature to that of the pure clusters. The pH_2O molecule appears to rotate freely in the cluster due to its large rotational constants and the lack of adiabatic following. The presence of pH_2O substantially quenches the superfluid response of pH_2 with respect to the space fixed frame. We also study the behaviour of a sulphur dioxide (SO_2) dopant in the pH_2 clusters. For such a heavy rotor, the adiabatic following of the pH_2 molecules is established and the superfluid renormalization of the rotational constants is observed. The rotational structure of the SO_2-(pH_2) clusters' ro-vibrational spectra is predicted. The connection between the superfluid response respect to the external boundary rotation and the dopant rotation is discussed. In comparison to the famous Andronikashvili bucket experiment on measuring bulk-phase superfluidity, the asymmetric top dopant is like a device with three different buckets in measuring the microscopic superfluidity.

Adaptive steered molecular dynamics (ASMD): Unfolding of Neuropeptide Y and decaalanine stretching

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The behavior and function of proteins necessarily occurs during nonequilibrium conditions such as when a protein unfolds or binds. The need to treat both the dynamics and the high-dimensionality of proteins and their environments presents significant challenges to theoretical or computational methods. The present work attempts to reign in this complexity by way of capturing the dominant energetic pathway in a particular protein motion. In particular, the energetics of an unfolding event can be formally obtained using steered molecular dynamics (SMD) and Jarzynski's inequality but the cost of the calculation increases dramatically with the length of the pathway. An adaptive algorithm has been introduced that allows for this pathway to be nonlinear and staged while reducing the computational cost. The potential of mean force (PMF) obtained for neuropeptide Y (NPY) in water along an unfolding path confirmed that the monomeric form of NPY adopts the pancreatic-polypeptide (PP) fold. [*J. Chem. Theory Comput.* **6**, 3026-3038 (2010); 10.1021/ct100320g.] Adaptive SMD can also be used to reconstruct the PMF obtained earlier for stretching decaalanine in vacuum at lower computational cost. [*J. Chem. Phys.* **136,** 215104 (2012); 10.1063/1.4725183.] The PMF for stretching decaalanine in water solvent (using the TIP3P water potential) at 300K has now been obtained using adaptive SMD. Not surprisingly, the stabilization from the water solvent reduces the overall work required to unfold it. However, the PMF remains structured suggesting that some regions of the energy landscape act partially as doorways. This is also further verified through a study of the hydrogen-bond breaking and formation along the stretching paths of decaalanine in vacuum and solvent.

Interference and Decoherence in Quantum Dynamics: Path Integral Renormalization, Semiclassical and Quantum-Classical Methods

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Interference effects are the essence of quantum mechanics, but are easily destroyed through thermal averaging or interaction with polyatomic environments. Forward-backward semiclassical dynamics methods take advantage of this quenching, allowing ac-curate and efficient simulation of such low-temperature fluids as para-hydrogen and su-perfluid helium.

Temporal and spatial locality is exploited to decouple variables in the path integral expression of quantum dynamical properties, leading to iterative formulations. In the ab-sence of memory, an iterative Monte Carlo approach has been developed that minimizes the instabilities associated with phase cancellation, leading to an exponential reduction of statistical error. Integrating out the degrees of freedom corresponding to a system's envi-ronment introduces an influence functional which contains memory interactions. The ob-servation that this memory tends to be short-lived led earlier to the development of itera-tive path integral methods, which have been used to study reaction rates and charge trans-fer processes. These ideas are extended to dissipative baths with very long memory and multiple time scales via a renormalization approach, which includes memory correlations through successively longer times.

Rigorous quantum-classical and quantum-semiclassical formulations emerge from path integral ideas. We propose accurate and practical methods for evaluating the result-ing expressions. These ideas allow simulation of nonadiabatic effects without requiring the mapping of the solvent on an effective harmonic bath.

Nanoscale Chemically-Driven Dimer

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Hydrodynamic interactions play an important role in microscopic biochemical systems. Strong fluctuations as a consequence of Brownian motion govern the dynamics of molecular machines operating in an environment such as the living cell. The microscopic dynamics of molecular machines, e.g. polymers or proteins in solution, may be studied in computer simulations using molecular dynamics.

Recent advances in general-purpose computing using graphics processing units (GPGPU), with peak single precision floating-point performances of multiple Tflop/s and an easily accessible programming interface in form of the NVIDIA CUDA toolkit, have brought about the rapid development of GPU implementations of computational algorithms in the field of biochemical simulations. The molecular dynamics package used in this study, HALMD, has demonstrated speed-ups over serial CPU implementations of up to two orders of magnitude.

This study on molecular machines focuses on a single dimer of nanometre size in the presence of a chemical gradient of atomistic solvent particles. Due to the small scale of the dimer, it is subject to strong thermal fluctuations. The initial goal of the study is to analyse a possible effect of the chemical gradient on the dimer dynamics, by comparing its dynamics to an equivalent nonreactive system.

In silico **construction of Metal Organic Framework materials for high throughput virtual screening and data mining of materials for CO_2 capture.**

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Metal Organic Frameworks (MOFs) are a class of nano-porous materials formed by the self-assembly of metal ions and organic linker molecules. One important application for MOFs involves using them as solid sorbents for low cost CO2 capture from coal burning power plants. Due to the diversity of organic linker molecules and metal centres there are nearly an infinite number of combinations of these secondary building units (SBUs), yielding MOFs with diverse chemical and physical properties. Recently, our group has automated the evaluation of the gas adsorption properties of MOFs for the virtual high throughput screening of the materials to aid in the synthesis new MOFs with specific properties. To take advantage of the virtual screening capability that is available, we have developed an algorithm to generate MOF structures from a library of metal clusters and organic molecules. The algorithm samples a subset of common structural and topological motifs, with known assembly based on experimental crystal structures. By interchanging organic and metal linkers and introducing new linkers of similar connectivity, we built and sampled a large database of generated structures with chemically feasible connectivity. We have used 12 metallic and 50 organic SBUs, along with 12 common functional groups to generate over 150 000 MOF structures which were screened for their CO2 capturing performance. To handle the large amount of data generated from screening these MOFs, a MySQL database was developed for data mining purposes in which queried information can be accessed quickly and easily.

Rapid reactivity prediction in direct arylation reactions using machine learning classifiers

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Transition metal-catalyzed direct arylation of (hetero)arenes constitute a tremendously powerful synthetic tool for a wide range of coupling partners to be combined efficiently. This approach for carbon-carbon bond construction allows assembling complex molecular frameworks of diversified interests encompassing medicinal chemistry, materials, and nanotechnology. However, designing site-specific direct arylation reactions remains challenging since most (hetero)arenes possess several C-H bonds. Although DFT calculations can successfully predict the regioselectivity through evaluation of the rate-determining transition state for each arylation site, this is time consuming. Therefore, simple computational models based on the substrate structures would represent feasible alternatives to the systematic reaction pathway calculations. Here we present the first chemoinformatic model for the fast and accurate prediction of reactive sites in cross-coupling reactions, derived from a set of 36 hetero-arenes with 130 potential coupling sites. We trained the models using only the Mulliken atomic charges on each coupling carbon and the charges on the two neighbouring atoms. As depicted in the Figure, the solid and dashed circles highlight the coupling carbons and the associated neighboring atoms, respectively. A Support Vector Machine (SVM) model successfully predicted the C-H coupling site with 80% accuracy. Using additional descriptors such as atom-type features resulted in even better models. The optimum SVM model is freely available online as a webserver application at http://titan.chem.uottawa.ca/crosscoup.
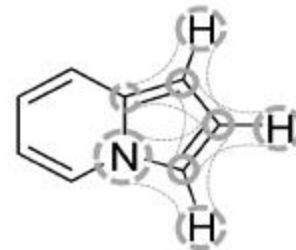
An Efficient Method for Transition State Optimization Using Redundant Internal Coordinates

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An important problem in studying chemical reactions computationally is optimizing the structure of transition states and stable intermediates. We have developed a new method for optimizing transition state and minima structures using redundant internal coordinates. The new methods is innovative because it allows the user to select a few key reduced coordinates, whose Hessian components will be accurately computed by finite differencing; the remaining elements of the Hessian are approximated with a quasi-Newton method. Usually the reduced coordinates are the coordinates that are chemically involved in bond breaking/forming. To test the efficiency of this program; a database of transition state structures has been examined, and the results have been compared to the standard algorithms from the Gaussian program.

An Exact Density-Potential Relation in Density Functional Theory: A Differential Virial Theorem

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The differential virial theorem (DVT) is an exact pointwise relation between the electron density, its derivatives, kinetic energy density and the external potential. We show that this theorem can be derived in three different ways: from the Kohn-Sham equations, from a hypervirial relation for the density operator, and from the equation of motion for the time-dependent paramagnetic current density. To illustrate the practical significance of the DVT, we employ it to construct Kohn-Sham exchange-correlation potentials from given electron densities.

Chemoinformatics based Modelling of Gas Adsorption Properties in Metal Organic Framework Materials

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Metal-organic frameworks (MOFs) are a class of porous solids formed by the self-assembly of structural building units - metal ions and polydentate organic linkers. MOFs have been targeted as potential enabling materials for vehicular storage of gaseous fuels and for CO_2 capture for clean energy applications. However, the large-scale discovery of MOFs with enhanced performance brings about a combinatorial design challenge that demands efficient experimental and computational screening tools. Here, we report the first large-scale Quantitative-Structure-Property Relationship (QSPR) analysis of the gas adsorption parameters of MOFs. The theoretical methane adsorption capacities of ~130,000 hypothetical MOFs from a database of hypothetical MOFs were correlated to structural features. Nonlinear SVM models predicted the theoretical methane adsorption capacities of the test set of 120,000 MOFs with R^2 values of 0.72, 0.88 and 0.95 at 1 bar, 35 bar and 100 bar. The models revealed that even higher methane capacities could be achieved at unexplored regions of void fraction and pore diameter, thereby providing design targets for new ultra-high performance MOFs. QSPR models of CO_2 uptake capacities were also developed using the radial distribution functions of the atoms in the MOF that yielded the most accurate predictions with R^2 values of 0.70. The QSPR approach also exhibited great potential to recognize CO_2 binding sites in MOFs with preliminary accuracy of 75%. Two webservers are freely available online at titan.chem.uottawa.ca/gadmof and /gadmof/BISILO to predict the methane uptake capacity and CO_2 binding sites in MOFs.

Molecular Dynamics Calculations of Activation Volumes of a Reaction Series: Mechanistic Applications

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A given reaction may proceed through several different mechanisms, each with its own transition state (TS). These TSs may have similar energies but different geometries and, as a result, different volumes. According to transition state theory, the activation volume is the difference between the volume of the TS and the reactants. Experimentally, activation volumes can be obtained from the pressure dependences of the rate constants:

$$-RT(\partial \ln k/\partial P)_T = \Delta V_{exp} = V_{TS} - V_R$$

By comparing the calculated and experimental activation volumes, one can pick a TS of the right "size" and thus elucidate the reaction mechanism by identifying the most likely reaction pathway. It has recently been shown by our research group that molecular dynamics simulations provide a suitable tool for theoretical calculations of activation volumes. In this project we focus on the calculation of the activation volumes for a series of reactions in which an alpha-hydrogen is abstracted from a substituted aromatic hydrocarbon by a bromine radical.

Evaporation and Condensation Dynamics in Small Charged Clusters of Water and Methanol

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Building on our previous work [C.D. Daub and N.M. Cann, *Anal. Chem.* **83**, 8372 (2011)], we have simulated small (up to 40 solvent molecules) clusters of water or methanol containing a single calcium, sodium, chloride or iodide ion. We study evaporation and condensation of solvent from these clusters in two systems: a) in vacuum, by initially preparing the cluster at varied temperatures, b) with a surrounding inert gas of different initial temperatures. These methods give us a convenient means to study the entire range of relevant cluster sizes, from the bare ion up to an bulk-like liquid-vapour interface. We report interesting data on evaporation and condensation dynamics and coordination numbers as a function of the cluster size. Our potential models include polarizability *via* Drude oscillators, and we provide new data for the re-parametrizations necessary to simulate ions in methanol within the Drude oscillator framework.

coord. # vs. cluster size, H_2O and MeOH
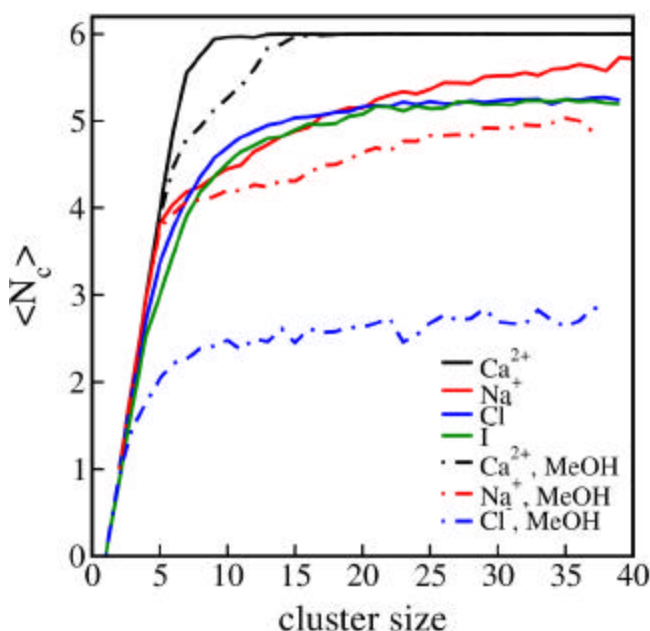
Binary atomic clusters Sn_mPb_n, $7 \leq m+n \leq 12$

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The Global Minima(GM) of the binary Sn_mPb_n atomic clusters, $7 \leq m + n \leq 12$, of all the possible stoichiometric ratios have been found using Taboo Search in Descriptor Space(TSDS) and DFT/PBE. The eects of the Spin-Orbit coupling have been included in the optimization for the lowest energy candidate structures and are shown to be important for the search of the GM not only to correct the total cohesive energy. All of the binary clusters form
substitution alloys with, apart from the 11-atom case, the pure clusters of the same size having the same ground state geometry. The relative energies of the isomers of the same cluster depend on (in order of decreasing importance) the overall geometry, the specic sites occupied by the two atom types and mixing/segregation. The clusters exhibit tendency for segregation for all species studied with the total cohesive energy dierence between the lowest energy homotops on the order of 0.02eV. The mixing/segregation trends are found to
be very dierent depending on the size of the basis set. The trends in the dipole moments for the lead-rich clusters agree with the experimental measurements and to a lesser degree for the tin-rich clusters with the absolute values being generally overestimated.

Optimization of van der Waals Parameters for Polarizable Force Fields

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A novel approach for optimizing van der Waals parameters of organic compounds is presented. The optimization is based on solving the nonlinear equations made up of the differences in interaction energies and the errors in 3 bulk properties: the self-diffusion constant, the density and the heat of vaporization. The resulting merit function is optimized in a two-step fashion by assuming that the bulk properties vary linearly with the parameters. This allows the interaction energies to be optimized between steps, which gives rapid convergence to the minimal merit function value. Structures for the interaction energies are obtained with a mixed molecular dynamics / Monte Carlo approach.

The quality of the parameters is tested by comparing hydration energies to experimental values. A significant improvement in the errors of the optimized parameters is shown both for the polarizable force field AMEOBA and for the standard AMBER force field. A software package is also provided for users to develop their own parameters.

On the Catalytic Effect of Ethers during Hydroboration of Alkenes

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Coupled-cluster and density-functional computations are used to test Brown's hypothesis (J. Am. Chem. Soc. **1982**, 104, 7148) for the catalytic effect of ether solvents upon hydroboration of alkenes. Two diboranes are tested: B_2H_6 and Brown's dimer (9-BBN)$_2$ (9-BBN = 9-borabicyclo[3.3.1]nonane, $C_8H_{15}B$, **Figure 1**). Comparisons to Brown's data are made for (i) infrared and ^{11}B-NMR spectral features, and (ii) an equilibrium constant for adduct formation. Transition-state searches were performed for four S_N2-type reaction steps, exploring a hypothesis published by Schleyer (J. Chem. Soc., Chem. Commun. **1983,** 606). We concur with Brown regarding the value for the equilibrium constant for adduct formation, and explain why this should not be computed with traditional gas-phase ΔG estimates from computational chemistry codes. All 4 S_N2-type transition states were located for B_2H_6 + tetrahydrofuran, but not all are expected to exist for the 9-BBN dimer due to steric hindrance for S_N2 approach.
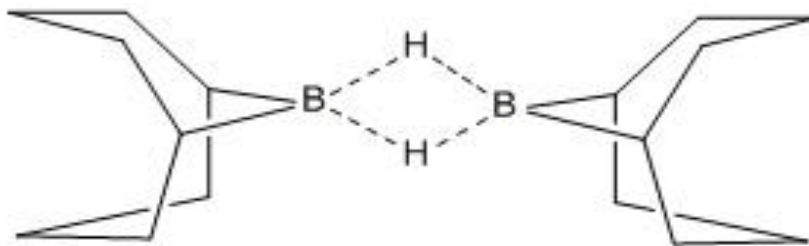
Silicate Polyol Complexes: A Window on Silicate Biochemistry

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Circumstantial evidence for the necessity of dietary silicon in the development of healthy connective tissue has been mounting for several decades. However, the role it plays has been rather elusive, partially due to the ubiquitous nature of silicates in aqueous envirnoments. Several years ago, Si-29 NMR evidence suggested that silicates only bind to sugar polyols that contain a specific stereochemistry. To understand this observation we performed a computational study on the binding of silicates to two four carbon polyols: threitol, which contains the appropriate stereochemistry, and erythritol, its diastereomer.

In this presentaion, our results from this study and the follow-up experiments that confirm our findings will be discussed. Additionally, our thoeretical study to assess a more recent proposal into a possible mechanism by which silicates may induce cellular communication will be described.

Using new quantum chemical methods to investigate NLO properties of linear hydrogen chains

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Conjugated molecular chains such as polyacetylene (alternating double and single bonds) or polyyne (alternating triple and single bonds) are materials of considerable interest to the chemical industry and material sciences as they exhibit large nonlinear optical (NLO) effects when exposed to electric fields.

Unfortunately, the quantum chemical description of these systems, and in particular the calculation of polarizabilities and hyperpolarizabilities, bears some insufficiencies when treated with conventional density functional and wave function theory. In recent investigations we were able to show that electron correlation has an enhancing effect on NLO properties for small chain lengths only, whereas in extended polymeric systems it turns into a damping contribution compared to uncorrelated calculations.

There is thus the need to look at the effects of electron correlation for long chains in greater detail. Linear chains of dimerized hydrogen can act as a simplification for conjugated systems which can be investigated to great accuracy using new approaches of quantum chemical methods such as matrix product state calculations or reduced density matrix theory.
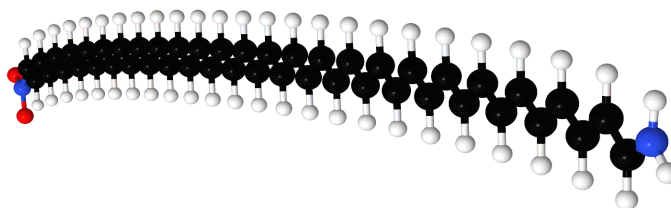
The routine construction of vibronic models and their applications to simulation of photoelectron and UV-visible absorption spectra

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The most common approach to simulating vibronic structure in electronic spectra is the harmonic Franck-Condon (FC) approach, which assumes the validity of the Born-Oppenheimer (BO) approximation. However, it has been known for some time that the FC approach is not accurate for systems where the states are close in energy and have complicated features such as avoided crossings and conical intersections. To create accurate spectra the effects of coupling between electronic states must be included. By including this coupling we go beyond the BO approximation. In a vibronic approach a potential energy matrix (PEM) is constructed in a diabatic basis. The Taylor series of the PEM is constructed from a set of electronic structure calculations in a set of displaced geometries and a suitable diabatization scheme. The vibronic coupling constants defining the PEM can be used to generate complete potential energy surfaces. These potential energy surfaces can be generated for ionized or excited states, and used to simulate photoelectron and UV-visible absorption spectra. The vibronic coupling models were constructed using an in house version of the ACES2 program and the VIBRON program created in Dr. Nooijen's group. Vibronic models have been constructed for twenty different small molecules, which shows that the process of simulating spectra while including non-adiabatic, vibronic coupling effects can be straightforward. The resultant spectra often show improved agreement with experimental spectra when compared to the spectra generated using the FC approach.

Stability and Electronic structure of Actinide(IV) Oxide Clusters of Zonohedral Geometry: A Relativistic DFT Study

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Recently, several stable, well defined actinide(IV) oxide clusters have been synthesized. These clusters are of importance as models of actinide(IV) colloids, which can be responsible for actinide environmental mobility. The clusters are also of interest as a route to new nuclear fuel materials and, for the Uranium, molecular magnets. The most frequently found U(IV) and Th(IV) clusters are of fluorite structure and An_6O_8 stoicheometry[1]. However, larger fluorite clusters of U10 and U16 as well as non-fluorite clusters of $U_{12}O_{20}$ were also prepared[2]. The known clusters of An_6O_8 type have rhombic faces with alternating An, O vertices. Polyhedra of such kind are called zonohedra. We explore, using DFT methods, lower and higher order zonohedra besides the $An_6O_8^{8+}$ rhombohedron: the cube $An_4O_8^{8+}$, and the triacontahedron $An_{12}O_{20}^{8+}$, and trace their stabilities to the smallest oxide cluster, An_2O_4 rhomb. For An=Th,Pa,U we show that, with a proper ligand environment compensating the charge, all these clusters are minima on PES; besides compensation of the charge, ligands are not crucial for the clusters' stability (bridging ligands are not mandatory and ligands of different kinds are interchangeable). For Pa, U we also explore the variety of spin states of the cluster, and show that the anti-ferromagnetic singlet state of the cluster is competitive with all-high spin state, depending on the clusters' ligands.

[1] Berthet, J.C.,et al. Chem. Comm.,**2005:** 3415. [2] Nocton, G., et al.Chem. Comm., **2010:** 2757.

Concerted and sequential proton transfer mechanisms in water-separated acid-base encounter pairs

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Acid-base reactions in water takes place in two steps: diffusion and reaction. The chemical event often involves the participation of an intervening water molecule bridging the acid to the base, whose precise role is controversial. Using first-principles molecular dynamics and computational time-resolved vibration spectroscopy it was found that neutralization can occur with or without formation of a reaction intermediate.
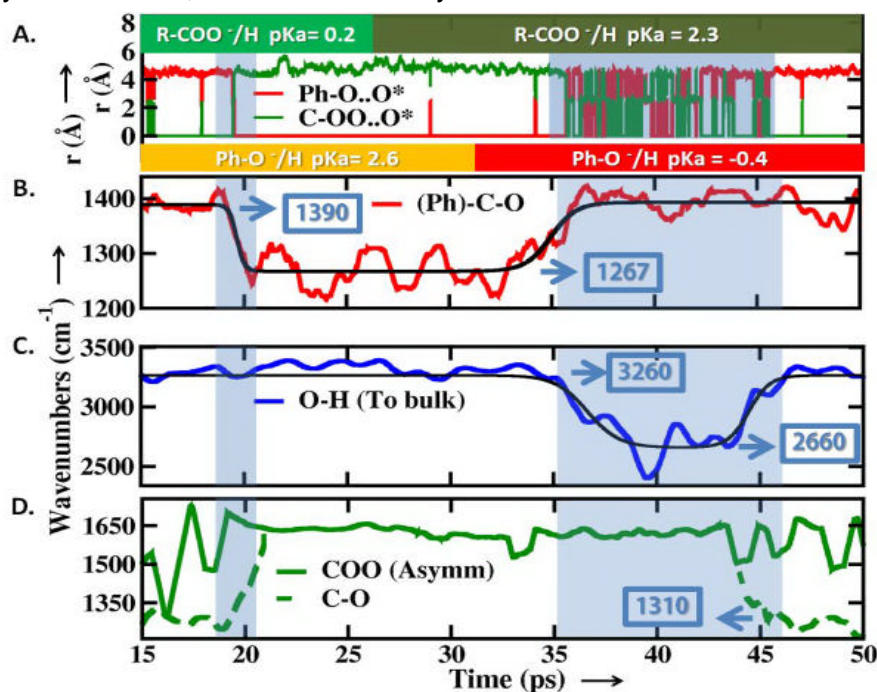
On the analytical representation of free energy profiles with a the Morse/Long-Range approach: application to the water dimer.

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We investigate the analytical representation of potentials of mean force (pmf) using the Morse/Long-Range (MLR) potential form. This is the first time that the (MLR) form has been used to represent free-energy surfaces. The water dimer with rigid monomers described by a classical Transferable Intermolecular Potential with Four Points (TIP4P) is used as a test case. We first calculated an "exact" pmf using direct Monte Carlos (MC) integration. We term such a calculation our gold standard (GS). Secondly, we compare our GS with several MLR fits to the GS to determine the quality of the fit. We then, obtain the water dimer pmf using Metadynamics simulations and we compare these simulations again to the GS and GS MLR fits. Finally, we calculate the rate constant for the water dimer dissociation process using the GS, the GS MLR fits, and the Metadymics MLR fits. Our results are in agreement with the literature, proving the suitability of the MLR potential form for representing free-energy surfaces. Our approach yields a compact and smooth representation of pmf data.

Methylarsenic Sorption onto Iron and Aluminum Oxides. A DFT Study.

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Dimethylarsinic Acid (DMA) and Monomethylarsonic Acid (MMA) are important organoarsenical compounds detected in arsenic speciation studies of environmental samples and synthesized during pyrolysis of oil shale. DMA and MMA have also been used as herbicides and pesticides and they have the potential to be transformed into more toxic forms of arsenic. Little is known about the interactions of these methylated arsenicals with iron and aluminum oxides which are reactive components of soils and ubiquitous in the environment.

Density functional theory (DFT) calculations are used to study the interactions of hydrated DMA and MMA with iron and aluminum oxide clusters, while Gibbs free energies of adsorptions are calculated to see which reactions are more thermodynamically favourable. Calculations were performed using Gaussian 09, running on Sharcnet, with the B3LYP functional and the 6-31G(d) and 6-311+G(d,p) basis sets. Solvation is simulated by adding explicit water molecules, as well as by using the integral equation formalism polarizable continuum model (IEFPCM).

Calculations indicate that formation of inner-sphere and outer-sphere complexation is thermodynamically favourable with inner-sphere bidentate complexes being the most favourable. Inter-atomic distances for DMA-Fe were calculated to be 3.30-3.45 Å for the inner-sphere monodentate and bidentate complexes and 3.18-3.33 Å for DMA-Al inner-sphere monodentate and bidentate complexes. Outer-sphere complexes are also shown to play an important role in the adsorption of methylarsenicals to iron and aluminum oxides.

Molecular Simulation as a Tool to Aid Interpretation of 67Zn Solid-State NMR for Characterisation of Guest-Host Interactions in Metal Organic Frameworks

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Metal Organic Frameworks (MOFs) are a novel class of materials being developed for a wide variety of applications including catalysis, drug delivery and gas separations. Although X-ray crystallography is an effective tool for characterising their structures, it remains a challenge to experimentally interrogate guest-host interactions and dynamic structural changes in MOFs. Because zinc is one of the most commonly used metals in MOFs, 67Zn solid-state NMR (SSNMR) should be an ideal tool to probe the Zn environment. Recently, the Huang group (Western) reported the first natural abundance 67Zn SSNMR study in several MOFs at ultrahigh field. Some spectra displayed unusual trends as a function of the composition of the guest mixtures. In order to interpret these results, we conducted long timescale molecular dynamics on a MOF with a variety of guest loadings to investigate how the Zn environment changes under different conditions. The dynamics of the mixtures provided information on guest mobility within the MOF. In addition, we developed a spatial distribution function which calculates angular distribution about symmetric directions. Coupling these two computational techniques correctly correlates changes in Zn environment with the obtained 67Zn SSNMR results, demonstrating that the combination of 67Zn solid-state NMR and molecular simulation can be a powerful tool for evaluation of the distribution and dynamics of guest molecules within MOFs.

An ab Initio Study of Iron(II) Hydration and Complexation with Chloride

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Atomic Energy of Canada Limited and CANDU are currently developing a Gen-IV Supercritical Water-cooled Reactor (SCWR). The SCWR offers advantages of increased thermal efficiency and sustainability, but at the cost of operating under extreme conditions (650°C and 25 MPa). Under these conditions, transition metals from the construction materials could dissolve (corrode) and form complexes with surrounding anions and reprecipitate on the pipes and valves of the reactor. Being able to predict and control the water chemistry inside the reactor is essential to ensuring the sustainability of the reactor. Iron is one transition metal of interest because it is a primary component of many metal alloys that are being considered for construction. Comprehensive ab initio computational studies were performed on iron(II) complexes containing water and chloride ligands. For all molecules studied, optimized geometries were obtained as well as vibrational stretching frequencies, which were compared to experimental data, where possible, so that predictions could be made with respect to the most likely species to exist inside the reactor.
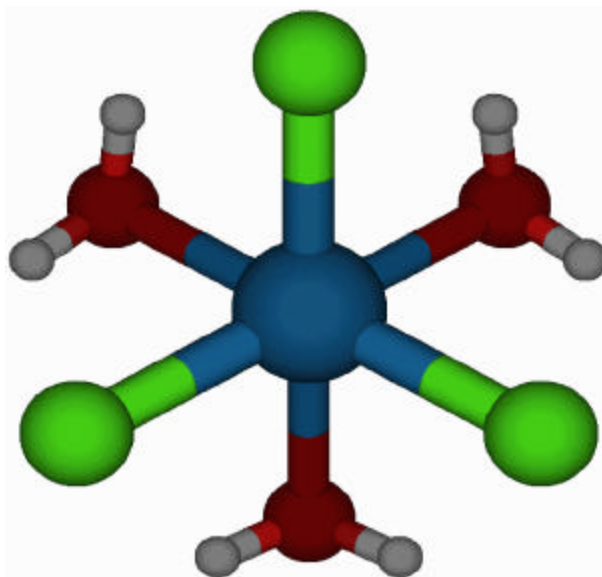
Chemometric Modeling of Catalyst Enantioselectivity by Molecular Orbital Descriptors

NR Trefiak, **M Fernandez** and **TK Woo**[*$] <twoo@uottawa.ca>, Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa.

We present a 3D Quantitative Structure Activity Relationships (3D-QSAR) method using quantum chemically generated descriptors for catalyst optimization. We examined 18 catalysts used for the asymmetric addition of diethylzinc to benzaldehyde, ranging in %e.e. from 0 to 98%. Unique to our study, we utilized quantum chemically derived descriptors based on the highest occupied and lowest unoccupied molecular orbitals (HOMO, LUMO) to correlate the catalysts' enantioselectivity to their electronic structure. The quantum chemical data at the van der Waals surface was treated with a data reduction method to generate so-called "correlograms" which form alignment-independent descriptors or "fingerprints" for the catalysts. A genetic algorithm was used to find the best "fingerprint" features to fit partial least squares regression of catalyst enantioselectivity. The optimum QSAR model outperformed previous reports yielding squared correlation coefficients (R2) of calibration, internal validation and test set prediction of 0.95, 0.93 and 0.96, respectively. Our 3D-QSSR method demonstrates the potential of deriving descriptors based on molecular orbitals, which can be applicable to any homogeneous catalysis system having some experimental selectivity data available.
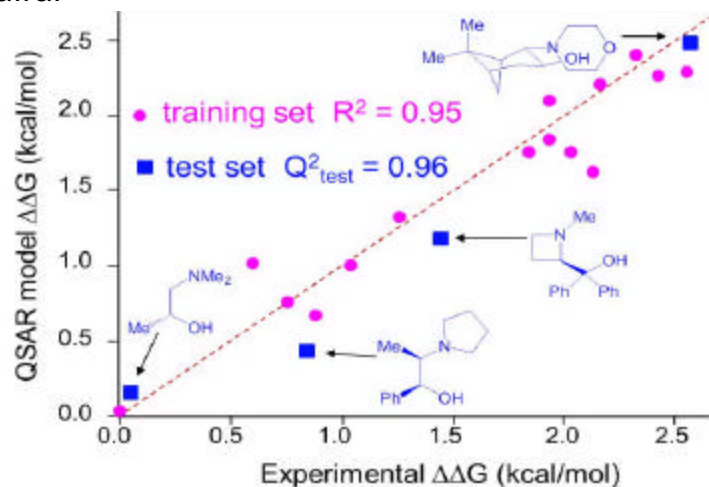
How Glutamine (Trojan horse) Deamidation Reaction induced Hyperammonemia: A Computational Approach

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Glutamine, a popular nutritional supplement, nontoxic amino acid, and an essential interorgan and intercellular ammonia transporter, can destroy the neurons' mitochondria like a Trojan horse. When glutamine enters into the mitochondria, in the presence of glutaminase it reacts with water and yields glutamate and excess ammonia which opens gates in the membrane of the mitochondria and thereby destroys it. The mechanistic details underlying the molecular basis of the catabolic production of excess ammonia remain unclear. Addressing this issue, both wavefunction and density functional theories are applied following several pathways by means of cyclic and direct approaches for glutamine deamidation in the gas phase, as well as in the condensed medium using PCM (polarizable continuum model) and SMD (solvent model on density) solvation models. The calculated activation barriers for cyclic hydrolysis pathways are rather high compared to the direct hydrolysis pathways. These findings also reveal that metabolic alkalosis may influence the glutamine deamidation since the direct hydrolysis of glutamine with OH^-/H_2O gives the lowest activation barrier, 103 kJ/mol at SMD with B3LYP/6-31+G(d,p). A stable network of hydrogen bonds in the transition state for this pathway promotes the effective proton transfer, and therefore makes this mechanistic route energetically the most favoured one.
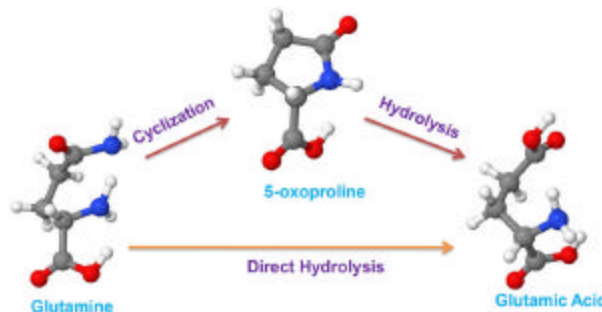
Computational Study of Blue Copper Protein Models

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Three copper complexes were evaluated to determine chemical properties and assess their potential as models for blue copper proteins. The model designed was trans-N-(2 pyridylmethylene) aniline, a tridentate chelate ligand and a Cu centre through thioether, imine and pyridine donor functionalities. The model was modified, creating two variants by replacing the pyridine pendant ring with pyrrole and imidazole pendant rings. These alterations were made to provide more data for analysis and new synthetic targets for chemists. Each individual model had its geometry optimized under three conditions, with the the oxidation state of copper as +1, +2 and finally as a free ligand. The models were optimized using B3PW91 as a theory level with the 6-311G+(d,p) basis set. To validate the computational method, the bond lengths and bond angles of two X-ray structures of similar Cu complexes were compared to models optimized under B3PW91 and 6-311G+(d,p) and were in good agreement. For each model the partial charges of each individual atom calculated. The oxidation energy for each of the compounds was calculated for gas phase. The solvation energies were calculated for each compound in various solvents under each charge condition outlined above. Using this data, the oxidation energy in each solvent was calculated and it was found that the energy it takes to oxidize the compounds is correlated with the pKa/dipole ratio of the solvent.
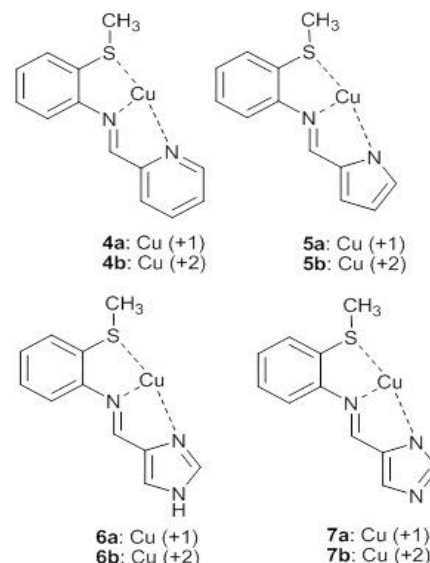
FA³PS A Code for Fully Automated Adsorption Analysis in Porous Solids for High Throughput Computational Screening

TD Daff <*tdaff@uottawa.ca*>, **PG Boyd**, **ES Kadantsev**, **M Fernandez Llamosa** and **TK Woo**[*$] <*twoo@uottawa.ca*>, Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa.

Carbon capture represents a serious strategy to mitigate the effects of greenhouse gas emissions from burning fossil fuels. Metal organic frameworks (MOFs) and other porous solids have the potential to replace current energy inefficient technologies. Using a suite of in-house developed computational tools we are able to fully analyse the adsorption properties materials from a periodic structure, with no user intervention. Our REPEAT method for accurate charges in periodic systems, Monte Carlo simulation code for gas adsorption capacity measurement, and binding site location and post analysis tools are seamlessly integrated with standard atomistic simulation packages in an adaptable manner by our FA³PS frontend to enable high throughput screening of thousands of new hypothetical structures or fine-grained simulation of experimentally characterised materials. Our post analysis will reveal the specific features of the sorbents that are required for different applications such as flue gas carbon capture or gas separation.
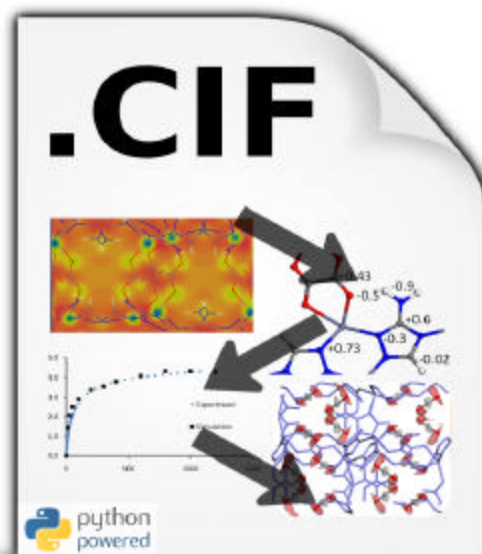
Computational studies of biofluorophores

A Brown[*$] <*alex.brown@ualberta.ca*>, Department of Chemistry, University of Alberta, Edmonton, AB, T6G 2G2.

I will discuss our recent computational work studying the photophysical properties of biofluorophores. We have examined using time-dependent density functional theory (TD-DFT) a series of structurally related 2,1,3-benzoxadiazole fluorophores and evaluated changes in their photophysical properties upon conversion from alkyne (or azide) to triazole forms.[1] The TD-DFT results consistently agreed with the experimentally determined absorption and emission wavelengths. Previously derived simple methods for predicting relative quantum yields were re-evaluated based on the new TD-DFT results and shown to be deficient. These results provide a necessary framework for the design of new substituted benzoxadiazole fluorophores. In the second half of the talk, I will present computations of the photophysical properties for a recently synthesized family of emissive RNA nucleobases.[2] These modified analogs are obtained by replacing the imidazole moiety of the RNA nucleobases with thiopene and represent a complete alphabet of emissive and isomorphic analogs derived from one heterocylic nucleus. An extensive study of absorption, emission and charge transfer character of these systems has been conducted.[3] The theoretical results reveal excellent agreement with the reported experimental data[2] as well as allow the comparison of excited-state properties with their naturally occurring RNA counterparts. [1] A. Brown, T.Y. Ngai, M.A. Barnes, J.A. Key, and C.W. Cairo, J. Phys. Chem. A 116, 46-54 (2012); [2] D. Shin, R.W. Sinkeldam and Y. Tor, J.Am.Chem. Soc. 38, 14912-14915 (2011); [3] M. Gedik and A. Brown, submitted.

Molecular shape and compression dynamics of polymer brushes.

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Polymer grafting is central for the design of surfaces resistant to wear, biosensors, and composite materials with special mechanical, thermal and electrical properties. Here, we use Brownian dynamics simulations to study the compressive behaviour of polymer mushrooms and brushes. We consider the case of a "clean" compressive surface, as well as an approaching surface which itself is a polymer brush. Polymers are simulated by using a bead-spring model that includes a variable persistence length (chain rigidity) and a Lennard-Jones interaction between monomers, over a range of chain lengths and grafted densities. In each case, we have analyzed how the degree of compression (and compression rate) affects chain size, asphericity, as well as the entanglement complexity within and between chains. The results show that, due to chain interpenetration, the presence of an upper brush introduces a qualitative change in chain size and entanglement with respect to the compression by a bare upper wall. Our results indicate that the interpenetration between layers depends on whether chains can reaccommodate rapidly with respect to the rate of compression by the top surface. We find that the degree of interbrush penetration increases for a while with growing confinement for short chains and low surface coverages, yet it becomes less important in denser brushes with longer chains, regardless of their flexibility. In this communication, we put these results in the context of the general behaviour of polymers under confinement.

The Next Generation of High-Quality Benchmarks for Non-Covalent Interactions

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In response to failures of approximate quantum-chemical methods for non-covalent interactions, a concerted effort by numerous theoreticians (in both wavefuntion and density functional communities) has led to several new or modified approaches which promise much more reliable results, including dispersion-corrected density functional theory (DFT-D), Becke and Johnson's exchange dipole moment (XDM) functional, non-local density functionals for dispersion, spin-component scaled versions of MP2 and CCSD, and various forms of symmetry-adapted perturbation theory. The best of these new approaches are now reaching an accuracy (mean absolute errors of 0.2 kcal/mol or less) that is becoming comparable to the error in many of the available benchmark values [1]. In addition, the behavior of the new methods can vary depending on the non-covalent interaction type (e.g., hydrogen-bonded, dispersion dominated, etc.) Hence, there is a critical need for a new set of benchmarks that are (1) of very high quality (errors of 0.1 kcal/mol or less, or even significantly less than this for a small number of cases where one wishes to "benchmark the benchmarks"), and (2) span a wide range of geometries, sizes, and types of interactions, to avoid coming to misleading conclusions about the performance of a method. This talk will outline our group's recent efforts at providing these required high-quality benchmarks for non-covalent interactions.

Substrate-Assisted Catalysis in Aminoacyl-tRNA synthetases: Insights and New Mechanisms From Computational Chemistry

JW Gauld[$] <*gauld@uwindsor.ca*>, Dept. Chem. and Biochem., University of Windsor, Windsor, Ontario, N9B 3P4, Canada.

Aminoacyl-tRNA synthetases (aaRS's) are a ubiquitous class of enzymes found in all living organisms. They are now thought to be involved in a diverse array of physiological processes including porphyrin biosynthesis, immune responses and inflammation. However, they are most well known for their critical role in protein biosynthesis. In this capacity they catalyse the activation of amino acids and subsequent transfer onto their cognate tRNA's. It is due in part to this crucial function at the interface between nucleic acids and proteins that they are thought to be quite ancient enzymes. Despite catalyzing the same mechanism, remarkably, they have been found to have remarkably diverse active sites. Furthermore, they are also devoid of an obvious catalytic base. As a result it has long been thought that they utilize a base within the substrate itself. Recently, a number of aaRS's have been found to contain metal ions within their active sites. However, the role of such ions remains unclear or unknown. Using a remarkably broad array of computational methods from Docking and MD to QM/MM, we have investigated the mechanisms and underlying rate-enhancing power of these enzymes.

A Tail of DNA Damage and Repair

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The overall objective of research performed in the Wetmore laboratory is to use a range of computational approaches better understand DNA damage and repair pathways. Despite its relatively simplistic structure, DNA contains all information vital to life. However, this crucial information can become damaged by exposure to external agents (X-rays, UV sunlight) or by natural processes (errors when DNA is copied). Since DNA repair has been correlated with the prevention of life-threatening illnesses, it is important to understand DNA damage and repair pathways, including how enzymes repair the damage in our bodies. This talk will provide a survey of some recent topics of interest such as damage to the guanine DNA nucleobase by phenolic-containing carcinogens, and repair of nucleobase deamination and alkylation by the corresponding DNA glycosylase repair enzymes.
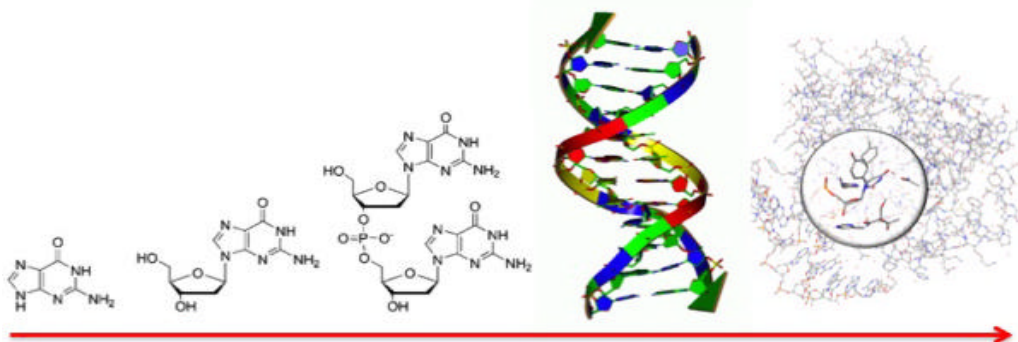
Atomic Energies and Richard Bader's Legacy

RJ Boyd *<russell.boyd@dal.ca>*, **L Albrecht** *<lauaralbrecht@dal.ca>* and **A Taylor** *<alexist@dal.ca>*, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3.

Richard Bader's name is synonymous with the quantum theory of atoms in molecules (QTAIM). His seminal contributions to the field began with a paper co-authored with Glenys Jones in 1963 (Can. J. Chem. 41, 586-606) entitled, "The Electron Density Distributions in Hydride Molecules. I. The Water Molecule", and continued for nearly 50 years. Bader's publications are among the earliest to recognize that the electron density plays a critical role in explaining and understanding many chemical phenomena. QTAIM provides unambiguous definitions of many properties related to the topology of the electron density. Bader's legacy includes a large number of terms such as molecular graphs, bond paths and critical points that are ubiquitous in the current literature. This presentation will focus on the analysis of internal stabilization of molecular complexes in terms of Bader's atomic energies, which are uniquely defined by QTAIM zero-flux surfaces. Two case studies will be discussed in some detail: the formation of guanine quadruplexes from a single-stranded telomere sequence (J. Phys. Chem. B 114, 9833-9839 (2010)) and the aggregation of water molecules into small clusters (J. Phys. Chem. A 116, 3946-3941 (2012)).

Quantum dots artificial atoms, large molecules or small pieces of bulk? Insights from time-domain ab initio studies

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Quantum dots (QD) are quasi-zero dimensional structures with a unique combination of solid-state and atom-like properties. Unlike bulk or atomic materials, QD properties can be modified continuously by changing QD shape and size. Often, the bulk and atomic viewpoints contradict each other. The atomic view suggests strong electron-hole and charge-phonon interactions, and slow energy relaxation due to mismatch between electronic energy gaps and phonon frequencies. The bulk view advocates that the kinetic energy of quantum confinement is greater than electron-hole interactions, that charge-phonon coupling is weak, and that the relaxation through quasi-continuous bands is rapid. QDs exhibit new physical phenomena. The phonon bottleneck to electron energy relaxation and generation of multiple excitons can improve efficiencies of photovoltaic devices. Our state-of-the-art non-adiabatic molecular dynamics techniques, implemented within time-dependent density-functional-theory, allow us to model QDs at the atomistic level and in time-domain, providing a unifying description of quantum dynamics on the nanoscale.

Some challenges in coarse-graining and multiscale modeling of macromolecular systems

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Because they develops on a wide range of length and timescales, structural and dynamical properties of macromolecular systems are difficult to study by atomistic computer simulations. To overcome these limitations, many descriptions of polymeric liquids with reduced internal degrees of freedom, or coarse-grained (CG) descriptions, have been proposed. This seminar is an overview of some unresolved questions in the field of coarse-graining and multiscale modeling of polymeric liquids (melts) and of our attempts to address them.CG models are derived by averaging out local degrees of freedom at a lengthscale shorter than a characteristic length, and obtaining in this way a new description in the coordinates of the resulting CG units, where the system interacts through an effective potential. The new CG description has the advantage that the length and timescale of the elementary step in the CG simulation are increased, the CG simulation accelerated, and the maximum length and timescales that the CG simulation can cover significantly extended. CG methods also have the disadvantages with respect to atomistic simulations of loosing information of the local scale, being thermodynamically inconsistent, and producing unrealistically fast dynamics. We have recently proposed a coarse-grained method, based on liquid state theory, where polymers are represented as chains of soft spheres. The simplicity of the model allows for analytical solutions of many of the relevant properties, both static and dynamic, and shows thermodynamic consistency for the CG model. A first-principle analytical procedure to reconstruct atomistic dynamics from CG simulations is presented and tested against experiments and atomistic simulations for polymer melts of different chemical structures, showing good agreement.

Modeling Electrospray Ionization: From flowing fluid to bare ions

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Electrospray ionization is a soft ionization technique that has revolutionized mass spectrometry especially for biomolecule analysis. Electrospray works by subjecting a flowing solution to a strong electric field. The optimal situation is for a fluid cone the Taylor cone - to form at the exit of a channel. A fine jet emerges from the cone, the jet breaks up to produce charged clusters, and the clusters eventually lose solvent leading to bare, unfragmented ions. Over the past decade there has been a trend towards the nano-scale regime where an increase in sensitivity allows for the analysis of very small sample volumes.
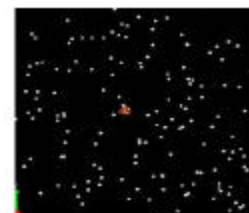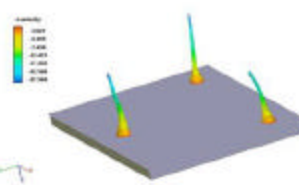
The talk will be divided into two parts.   In the first part, results from full-dimensional computational fluid dynamics simulations, based on the leaky-dielectric model will be presented. Single- and multi-channel electrospray is simulated and compared with experiment.   The role of contact angle, fluid conductivity, number of channels, channel separation and placement, field and flow rate are examined.

The second part of the talk will focus on the final stages of the process, where the ion loses its last remaining solvent molecules. Results from molecular dynamics simulations of charged clusters in the presence of an electric field and a buffer gas will be discussed. The role of field strength, gas pressure, and gas temperature have been explored.   The mechanism of solvent loss direct collision vs evaporation will be considered. The talk will conclude with recent results from a comparison of charged water and methanol clusters with various ions.

Much ado about icebergs: Hydrophobicity, water and the iceberg model

M Karttunen *<mikko.karttunen@uwaterloo.ca>*, Department of Chemistry, , University of Waterloo.

I will discuss the importance of hydration and water in biological systems, and address the classical Iceberg model of Frank and Evans. First, I focus on hydrophobic hydration using ab initio simulations and the relation to femtosecond spectroscopy measurements, and the consequences to protein and other systems [1]. I will then address the importance of hydration and dynamics of water by using docking properties of drugs - beta blockers - via atomistic molecular dynamics simulations as an example [2].

[1] Long-time correlations and hydrophobe modified hydrogen bonding dynamics in hydrophobic hydration, J.T. Titantah, M. Karttunen, J. Am. Chem. Soc., 134, 93629368 (2012)

[2] Molecular docking, multiple sequence alignment and atomistic molecular dynamics simulations reveal residues associated with selective binding of beta-blockers to human beta-1 and beta-2-adrenergic receptors, K. Kaszuba, T. Rog, K. Bryl, I. Vattulainen, and M. Karttunen, J. Phys. Chem. B 114, 8374-8366 (2010).

An improved method for extending the STO-NG basis sets to all elements of the periodic table

JP Ferguson and <u>**CC Pye**</u>[*$], Department of Chemistry,, Saint Mary's University, Halifax, NS B3H 3C3.

Current computational chemistry research is limited to examining molecules which contain elements of the first five periods of the periodic table, as the majority of popular basis sets are only available for these elements. The STO-NG basis sets are simple yet effective as economical method of obtaining initial geometries, wavefunctions, and force constants for improving the convergence behavior of subsequent computations. The development of a simple method for obtaining orbital exponents and expansion coefficients for the STO-NG basis sets with N=1-6 will allow for the extension of these basis sets to elements

of the entire periodic table. The existing method developed in our group was simplified with the use of new functions for the evaluation of complicated least-squares integrals to improve the efficiency and reproducibility of the calculations. Gaussian expansions of Slater-type atomic orbitals were found by least-squares analysis using Microsoft Excel for all orbital types up to 7p. All orbitals up to 5f were compared to the current accepted expansions. For the cases with N>3 the errors obtained were usually larger than the expected values by an order of magnitude. In most cases for N<=3 the results were identical, indicating that the method works for smaller expansions. New expansions were found for the 6s, 6p, 6d, 7s, and 7p orbitals.
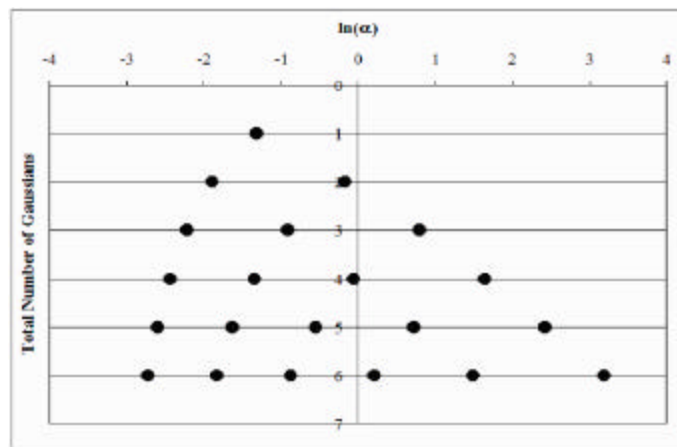
Dynamics of Conformational Modes in Biopolymers

<u>**M Stepanova**</u>[*$a,b] <*maria.stepanova@nrc-cnrc.gc.ca*> and **A Potapov**[b] <*apotapov@ualberta.ca*>, [a]National Institute for Nanotechnology NRC, [b]The University of Alberta.

We suggest a novel formulation of soft matter theory that paves the way to the understanding of the fundamental "design rules" that determine the structure and function of biological bolymers such as proteins [1]. Many roles that proteins and other biopolymers play in the cell are crucially dependent on their structure, which is thremendously complex. Thus the structure of proteins is strikingly different from better-understood substances composed of many similar molecules such as crystals or liquids. In contrast, individual protein molecules generally do not possess a periodic arrangement, are prone to changes in structure (conformation), but also cannot be described as a liquid. In this work, we have devised a rigorous way of representing real-time conformation changes and predicting the properties that remain stable (invariant) in individual protein molecules. The novel framework could be employed to characterize the stable structural properties of proteins from short molecular dynamics simulations. The theory also enables researchers to develop faster, more efficient and robust models for real-time biomolecular structure evolution than those presently available. The outcomes of the work may have profound implications for structural molecular biology, protein engineering, design of new drugs, and curing diseases related to protein misfolding. Applications of the framework are discussed.

[1] A. Potapov and M. Stepanova, Conformational modes in biomolecules: Dynamics and approximate invariance, Phys. Rev. E 85 (2012) 020901(R).

Modeling core/shell and alloy nanoparticles as oxygen reduction catalysts

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Better oxygen reduction catalysts are needed to improve the efficiency and lower the cost of fuel cells. Metal nanoparticles are good candidates for new catalysts because their catalytic properties are different from bulk metals, and are sensitive to particle size, shape and composition. The electronic structure can be determined for small particles, making it possible to optimize particles for a desired reaction. Here, we calculate the electronic structure of 1 nm core/shell particles and show how the energy of electrons in the shell can tune the binding of oxygen by varying the core metal. Transition state calculations for O_2 dissociation on the nanoparticle surface show that the d-band center is a good measure of the activation and reaction energies. Two factors are found to be significant for determining the catalytic activity of small nanoparticles; charge transfer in core/shell particles and the rigidity of alloy particles.
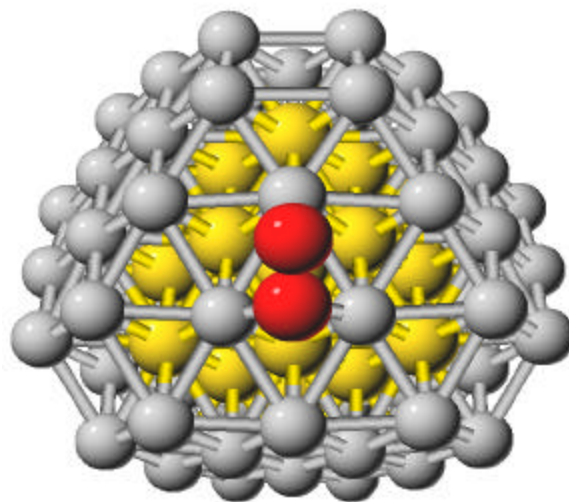
Quantum non-adiabatic dynamics through conical intersections: Model Hamiltonians and beyond

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One of the prevalent non-adiabatic features responsible for radiationless electronic transitions in large molecules of biological and technological significance is conical intersection topology. Conical intersections give rise to irreducibly quantum behavior which makes it impossible to use well established molecular dynamics techniques based on the Born-Oppenheimer approximation. In this talk, I will discuss some of the recent efforts in building simple, non-empirical, and accurate rate theories for describing non-adiabatic dynamics involving conical intersections. Starting from the linear vibronic model Hamiltonian and treating linear diabatic couplings perturbatively we have developed a simple analytical expression for evolution of electronic populations at finite temperature. The derived expression can be seen as a nonequilibrium generalization of Fermi's Golden Rule, and it has become a cornerstone of further extensions beyond linear vibronic coupling model Hamiltonian within a framework of direct quantum dynamics with Gaussian wave-packets.

Mixed quantum-classical Liouville simulation of nonlinear optical response in the mapping basis using the equation-of-motion phase-matching approach

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The equation-of-motion phase-matching (EOM-PMA) approach [J. Chem. Phys. 131, 194103 (2009)] provides an efficient way for simulating the response of a system to weak laser fields of arbitrary shape. In principle, this approach can be combined with any EOM for the time evolution of a system's density matrix or dipole moment. Within this approach, we introduce the mixed quantum-classical Liouville (MQCL) equation in the mapping basis for simulating the time-dependent response of a quantum subsystem coupled to a classical bath to N coherent laser pulses. In this basis, the resulting EOMs for the quantum and classical variables assume classical-like forms, thereby providing an alternative way for simulating the nonadiabatic dynamics of observables that does not involve surface-hopping. We demonstrate the use of this MQCL-PMA approach for the calculation of the transient absorption signal and the population of the photo-excited donor state in a model condensed phase electron transfer reaction.

A Kohn-Sham-Like Model for the 1-Body Reduced Density Matrix from a Strongly-Correlated Reference

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Kohn-Sham density functional theory (KS-DFT)[1] is a very popular approach to approximating the many-body Schrödinger equation due to its favourable speed and moderate accuracy. A non-interacting reference state (Slater determinant) which reproduces the correct electron density is employed. A correction term is then added to connect the fictitious non-interacting system to the real physical system of interest. Unfortunately, this correction term is unknown, and likely unknowable.
We present a method in the spirit of the KS approach using the 1-body reduced density matrix (1-RDM) as the fundamental variable rather than the electron density. A strongly-correlated reference state[2] is employed to achieve this result. Two different approaches to achieve this goal will be presented which are able to treat open- and closed-shell systems. These approaches are able to reproduce both the non-interacting and strongly-correlated limits.

[1] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965)
[2] R. W. Richardson, Phys. Lett. 3, 277 (1963)

Bimetallic cage clusters.

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We did DFT calculations (PBEPBE functional, LANL2DZ basis set) on twenty-four 10-atom clusters and fifteen 12-atom clusters with formula A_xB_y, with x+y=10 or 12, and A and B are metals from group 1, 2, 11, 12, 13 or 14 of the periodic table. The chemical composition of the clusters was chosen to satisfy an electronic shell closing criterion in the jellium model, with the number of valence electrons being 18 or 20. We performed an unbiased search for the global minimum (GM) in each case with the Taboo Search in Descriptor Space method. None of these clusters contains gold, which has a well documented propensity to form cages. Yet, surprisingly, 7 out of the 15 12-atom clusters have the icosahedral cage as their GM! Also, 5 out of the 24 10-atom clusters have cage-like structures. The 12-atom cluster cages are large enough to accomodate a central dopant atom with an atomic radius varying roughly between 0.7 and 1.3 Angstrom. Based on this geometric criterion alone, there are many possible dopants: most of the main group elements, and several metallic elements (Be, Cr, Mn, Fe, Co, Ni, Ga, Ge, and maybe Cu). I will show the most significant GM, low-energy isomers, and geometric descriptors that help classify the various structures.

The Oxidative Power of Key Intermediates in the Formation of Ovothiol.

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In several heme- and non-heme-iron-enzymes the $Fe^{IV}=O$ species is a competent oxidant and in fact is generally considered the ultimate oxidant. However, recent, evidence points to the possibility of a Fe^{III}-superoxo species acting as an active oxidant in select enzymatic reactions. Importantly, both of these reactive intermediates exist during the synthesis of ovothiol (OSH). OSH is an aromatic thiol that acts as an antioxidant providing a line of defense against reactive oxygen and nitrogen species. In the proposed mechanism (Scheme), formation of this thiol initially occurs with Fe^{III}-superoxo attacking a cysteinyl sulfur with concomitant O-O bond cleavage forming an oxo-ferryl species and sulfoxide. It is the $Fe^{IV}=O$ species that is then proposed to oxidize a histidine residue forming a histidyl radical that subsequently attacks the sulfoxide to form the desired histidyl-sulfoxide product. However, calculated redox potentials seem to indicate that the oxo-ferryl species is not suitable to oxidize the histidine residue. Therefore alternative paths were investigated. Some preliminary results will be presented.
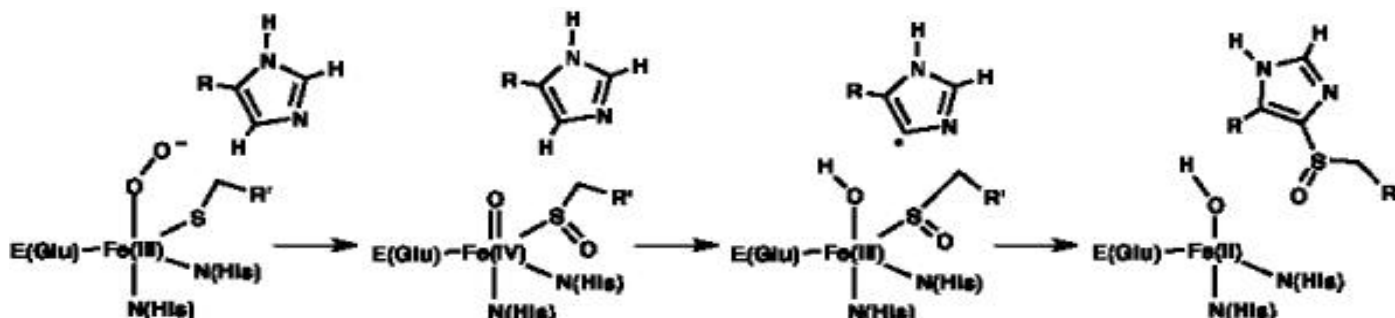
The Origin of the Conductivity Maximum in Molten Salts

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Density functional theory based molecular dynamics simulations of molten $BiCl_3$ and $SnCl_2$ were carried out in order to explore the maximum in conductivity found by experimentalists Grantham and Yosim. They believed that "ion association" at low densities contributed to the maximum, which Tödheide quantified with a degree of dissociation parameter and an assumption that "ion association" meant a shift in equilibrium from simple ions (such as $BiCl_2^+$ and $BiCl_4^-$) towards neutral molecules at higher temperatures. The simulations do not agree with the Tödheide hypothesis, and a new theory is presented where the conductivity is due to ions hopping from counterion to counterion based on a density-dependent Arrhenius equation. The conductivity maximum arises from competing effects between the frequency prefactor A, which describes the number of hopping opportunities, and the activation energy E_a needed for an ion to successfully hop between counterions. This theory was applied to the simulations and experimental data of molten $BiCl_3$ and $SnCl_2$, along with other simulation techniques and conductivity estimates, in order to understand the conductivity maxima further.

Le-PIGS: a novel method for ground state property prediction

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Nuclear ground state methods have been successfully employed in the study of low temperature systems such as superfluid helium droplets[1]. Such methods have been typically based on a Monte Carlo formalism, such as Diffusion Monte Carlo (DMC)[2] and Path Integral Ground State (PIGS)[3] Monte Carlo. Recently Ing et. al. have reformulated the PIGS method to utilize Molecular Dynamics sampling instead of Monte Carlo, which obviates the need for system-specific move construction (improved generality)[4]. In order to increase the statistical efficiency of phase space sampling via PIGS-MD, a modified Path Integral Langevin Equation (PILE)[5] has been adopted. This hybrid Langevin Equation Path Integral Ground State (LE-PIGS) method has demonstrated accurate results for a variety of sample systems, and is immediately generalizable to any system that can be studied via MD.

1 J.E. Cuervo and P.-N. Roy, J. Chem. Phys **125,** 124314 (2006).
2 B. Hetényi, E. Rabani, and B.J. Berne, J. Chem. Phys **110,** 6143 (1999).
3 A. Sarsa, K.E. Schmidt, and W.R. Magro, J. Chem. Phys **113,** 1366 (2000).
4 C. Ing, *Path Integral Langevin Dynamics of Complex Molecular Systems* (2011)
5 M. Ceriotti, M. Parrinello, T.E. Markland, and D.E. Manolopoulos, J. Chem. Phys **133,** 124104 (2010).

A Self-Interaction Correction Scheme for Approximate Kohn-Sham Potentials

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Exchange-correlation potentials derived from conventional density-functional approximations fail to reproduce the Coulombic (-1/r) decay. This problem is closely related to the self-interaction error and leads to incorrect description of response properties. We show that the self-interaction error in approximate Kohn-Sham potentials can be substantially reduced by fractionally depopulating the highest occupied molecular orbital level. Using shape-corrected semilocal potentials, we obtain excellent vertical ionization energies and Rydberg excitations from standard density-functional methods.

Pressure-induced phase transitions in crystalline diborane deduced by comparison of simulated and experimental infrared and Raman spectra.

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We have investigated the pressure-induced phase transitions in crystalline diborane by calculating the infrared and Raman spectra of eleven candidate structures at several pressure points, from ambient pressure to 50 GPa. The calculated spectra are compared with the experimental ones of Song et al. [Y. Song, C. Murli and Z. Liu, J. Chem. Phys. 131, 174506 (2009), C. Murli and Y. Song, J. Phys. Chem. B 113, 13509 (2009)]. One phase transition from β-diborane to another dimer structure *(P21/c)* is identified between 5.4 and 6.4 GPa. Our calculations indicate that the spectra of the latter structure remain in agreement with the experimental ones up to around 50 GPa. Calculated infrared and Raman spectra of the other 9 candidate structures, including ones with trimer, tetramer and polymer motifs are not consistent with the experimental data, despite the fact that the enthalpies of some of them are lower than β- or *P21/c*-diborane.

Molecular Docking Study of Fk506-binding Protein 35

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Peptidyl-prolyl *cis/trans* isomerases (PPIases) are a powerful enzyme superfamily capable of the rapid interconversion of *cis* and *trans* amide bonds involving proline amino acids in polypeptide chains[1]. The PPIases to be studied, Fk506-binding protein 35 (FKBP35), are found in *Plasmodium vivax* and *Plasmodium falciparum*, two protozoan parasites responsible for malaria transmission[2]. The current treatments for malaria use drugs that are non-specific and very toxic to humans[3]. Furthermore, the *Plasmodium* parasites have become resistant to the existing drugs. The goal of this work is to find a new treatment for malaria, one which shows little resistance to new drugs and has no side effects for the patient. This presentation will focus on the results obtained from a molecular docking study performed comparing previously-synthesized drugs and their binding affinity to PvFKBP35, PfFKBP35 and the most prevalent PPIase in the human body, hFKBP12.

1. Fischer, S.; Michnick, S.; Karplus, M. *Biochemistry*. **1993**, 32, 13830.
2. Alag, R.; Qureshi, I. *Prot. Sci.* **2010**, 19, 1577.
3. Malaria Report 2010. World Health Organization; **2010**.

A DFT Assessment of Ovothiol and Ergothioneine Binding to Copper

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Copper is well known to have a number of important roles in biological systems. However it is also known to damage key biomolecules via its redox abilities. In particular, the redox cycling between Cu(I) and Cu(II) creates reactive oxygen species (ROS) which can oxidatively stress DNA and proteins. Antioxidants such as Ovothiol (OSH) and Ergothioneine (ESH) can protect against this damage by scavenging ROS. Moreover, these mercaptohistidines can bind to the copper ions themselves, thus creating redox-inactive Cu-complexes. Unfortunately, how such species bond Cu(I) and Cu(II) to protect against oxidative damage is unclear. A range of DFT methods have been employed to computationally investigate the chemical characteristics of OSH-Cu and ESH-Cu complexes. Some results of this study will be presented.

An ab initio investigation of the hydration of the d^0 transition metal tetraoxo compleses

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The aqueous solution chemistry of simple oxometalates can be very complex and extremely important to understand experimentally and to describe computationally. The solvated oxometalate anion is considered to be surrounded by successive layers of the solvent water molecules creating a series of hydration shells, or spheres. This study is an examination of the first (innermost) hydration sphere of oxometalate species and the effect of the hydration sphere on the structure of the oxoanion. Ab initio calculations, using HF, MP2, and B3LYP levels of theory and extended basis sets including polarization and diffuse functions, were systematically performed to calculate the optimized geometries and vibrational spectra of the hydrated anion. The results of the calculations were compared to experimental values where possible. A correlation between hydration number and bond distance was routinely observed. Most frequently this relationship was the increase in bond distance between the anion and water molecules. In general it was found that with increasing oxidation number of the central metal atom on the anion, the metal-to-oxygen bond distance decreased. This is attributed to an increase in the level of sigma-interaction, and is supported by the predicted increase in corresponding symmetric stretch vibrational frequency of the tetrahedral CrO_4^{2-}, MnO_4^-, and neutral FeO_4.
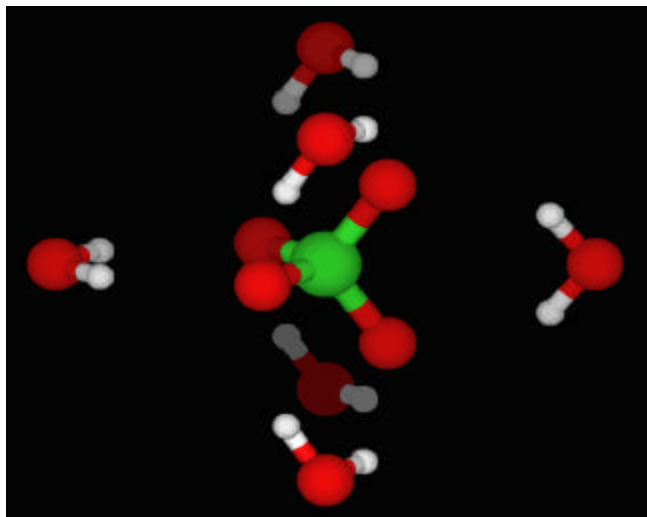
Metal-free deamination by the Zn(II)-containing metalloenzyme Nicotinamidase? A QM/MM Study.

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A major biochemical pathway within cells and organisms is the deamination of biomolecules. Indeed, this important reaction is key in many physiological pathways such as ion regulation in eyes, degradative pathways, and biomolecule modification. In particular, the deamination of nicotinamide to give nicotinic acid is central to the NAD^+ salvage pathway. Within many pathogenic bacteria, this reaction is catalyzed by the zinc-containing enzyme nicotinamidase. The Zn(II) ion is situated within the active site. Remarkably, however, in contrast to most other Zn(II) C-N bond hydrolyzing enzymes, it is thought to play no role in the catalytic mechanism. We have employed ONIOM QM/MM methods to investigate the mechanism and importantly, the role of the various active site cofactors and residues. In this poster some of our results will be discussed.
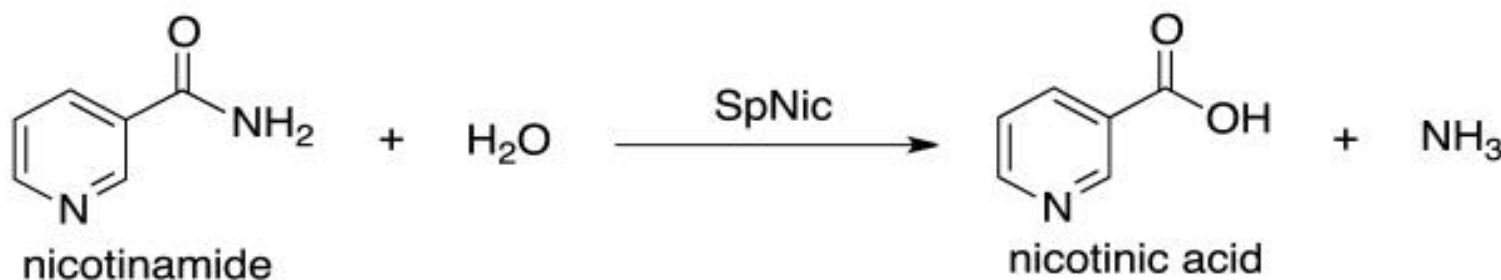
nicotinamide + H₂O →(SpNic) nicotinic acid + NH₃

A molecular simulation study of water vapour adsorption in metal organic framework materials

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Metal organic frameworks (MOFs) are materials composed of metal ions coordinated to organic molecules that can form three-dimensional nano- and mesoporous structures. MOFs with ultra-high internal surface areas have been found to selectively, and reversibly physisorb CO_2 with record capacities. Thus, they have received considerable attention because of their potential application as solid sorbents in combustion flue gas CO_2 scrubbing systems. However, one area that has not been broadly examined, is the stability and CO_2 capture ability of MOFs in the presence of water vapour, a primary combustion product. Even for MOFs that are stable in humid conditions, very few studies of the water adsorption properties have been published. In this work, we examine the accuracy of common water force fields (SPC, TIP3P, TIP4P-Ew, TIP5P) for reproducing the experimental water adsorption isotherms on both hydrophobic and hydrophilic MOFs. Our grand canonical Monte Carlo simulations reveal that water adsorption in hydrophobic and hydrophilic MOFs are considerably different from each other. Hydrophilic MOFs gradually uptake water, whereas hydrophobic MOFs show rapid water uptake at the saturation pressure. We also examine how CO_2 and N_2 adsorption is affected by the presence of water vapour and what implications water may have on the uptake capacities and selectivities in MOFs.

Centroid Effective Potential Approach to The Simulation of Large Parahydrogen Clusters and Droplets

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The quantum simulation of large molecular system is a formidable task. We explore the use of effective potentials based on the Feynman path centroid variable in order to simulate large quantum clusters at a reduced computational cost. This centroid can be viewed as the "most" classical variable of a quantum system. Earlier work has shown that one can use a pairwise centroid pseudo-potential to simulate the quantum dynamics of hydrogen in the bulk phase at 25K and 14K [Chem. Phys. Lett. 249, 231, (1996)]. Bulk hydrogen, however, freezes below 14K and we rather focus on nanodroplets in the very low temperature regime in order to study the superfluid behaviour of hydrogen. The calculation of the effective potential will be discussed along with its use in the context of molecular dynamics simulations. Centroid structural properties will be presented and compared to the results of path integral Monte Carlo simulations.

We will present an approach to de-convolute centroid structural properties in order to obtain real space results for hydrogen clusters of a wide range of sizes. The extension of the approach to the treatment of confined hydrogen will be discussed.

Molecular Dynamics Simulations on Various Weakly Bound Water-Parahydrogen Systems at Low Temperature

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We report Path Integral Molecular Dynamics (PIMD) studies on the low temperature properties of weakly bound clusters. We use a new version of the Molecular Modeling Toolkit (MMTK) with an implementation of the Path Integral Langevin Equation (PILE) thermostat. Our focus is on the low temperature dynamics of parahydrogen clusters with a non-rotating water dopant molecule. We also extend our study to the reverse case where hydrogen is doped in a water cluster and the low temperature properties of parahydrogen clusters within water clathrates are explored. These systems are of great interest in the context of hydrogen storage. We compare our PIMD results to those of more traditional Path Integral Monte Carlo (PIMC) methods. Future applications include an extension of the PIMD approach to zero temperature using the so-called Path Integral Ground State (PIGS) approach. The technique is analogous to Diffusion Monte Carlo (DMC) but with important differences that will be presented. Another extension includes using Ring Polymer Molecular Dynamics (RPMD), from which we can perform real time dynamics. We wish to obtain transport properties and rovibrational spectra using this technique.

An Investigation of Metalloporphyrins Containing the First Six *3d*-Transition Metals

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Metalloporphyrins are incorporated into protein structure ubiquitously in nature. The most well-known and abundant example is the iron-containing class of proteins known as heme proteins, capable of a vast array of chemical processes including oxygen transport, catalysis, electron transfer and active membrane transport. The incorporation of metal ions is crucial for many proteins as it provides the catalytic and electron transfer functionality. Recently in the literature there have been successful reports of the modification of the metalloprotein structure to achieve efficient cataylic activity.[1-3]

This study aims to systematically investigate the structural and electronic properties of the metalloporphine structure ligated with an imidazole group. More specifically, the first six 3d-transition metals are considered, each with various multiplicity and charge states. Density functional theory (DFT) and the Quantum Theory of Atoms in Molecules (QTAIM) are employed to investigate structural and electronic binding properties. Trends will be discussed and caparisons made to the iron-porphine structure.

1.Miner, K. D.; Mukherjee, A.; Gao, Y.-G.; Null, E. L.; Petrik, I. D.; Zhao, X.; Yeung, N.; Robinson, H.; Lu, Y. *Angew. Chem. Int. Ed.***2012**, 51, 1-5.
2.Zastrow, M. L.; Peacock, A. F. A.; Stuckey, J. A.; Pecoraro, V. L. *Nat. Chem.***2012**, 4, 118-123.
3.Larson, R. W.; Wojtas, L.; Perman, J.; Musselman, R. L.; Zaworotko, M. J.; Vetromile, C. M. *J. Am. Chem. Soc*. **2011**, 133, 10356-10359.

Development and Benchmarking of a Density-Functional Approximation for Noncovalent Interactions

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The accurate description of noncovalent interactions including dispersion is an important aspect of computational quantum chemistry with special relevance in biochemistry, condensed matter physics, and materials science. However, standard semi-local density-functional theory (DFT), the most widely used electronic structure method, fails for the dispersion interaction.

Becke and Johnson have developed a nonempirical density-functional approximation for the dispersion interaction known as the exchange-hole dipole moment (XDM) model, which we have combined with standard functionals for exchange and correlation to yield the PW86PBE-XDM method for noncovalent interactions. This presentation will outline further development of PW86PBE-XDM, including parametrization in the complete basis set limit and investigation of its basis-set dependence. Comprehensive benchmarking of intermolecular interaction energies is performed at both equilibrium and non-equilibrium geometries using the S22 S66, S66x8 and S66a8 benchmark sets of Hobza and coworkers. Intramolecular interactions, conformational energies and hydrogen bonding are investigated using the GMTKN30 database of Grimme and coworkers. With minimal empiricism, the PW86PBE-XDM method is found to accurately describe noncovalent interactions from rare-gas diatomics to large biochemical systems, both in the CBS limit and using standard Gaussian basis sets.

Predictions of the Geometries and Fluorescence Emissions of Selenium Oxyluciferins

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Predictions of the Geometries and Fluorescence Emissions of Selenium Oxyluciferins
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Email: xran@ uoguelph.ca

ABSTRACT: The absorption and emission spectra of the selenium oxyluciferin in Keto-Enol-Enolate and Phenol-Phenolate forms were systematically investigated. The geometries as well as the absorption and emission spectra of the selenium oxyluciferins were compared with those of the sulfur oxyluciferins. The ground state geometries were optimized by M06HF/6-31+G(d) and the absorption spectra were calculated by TDDFT//B3LYP/6-31+G(d). The excited state geometries and the emission spectra were studied by TDDFT//B3LYP/6-31+G(d). All the calculations were performed in a PCM model of dimethylsulfoxide (DMSO). It was demonstrated that the absorption and emission wavelengths of the selenium oxyluciferin were red-shifted compared with sulfur oxyluciferin.

Figure 1. Sketches of sulfur oxyluciferin and selenium oxyluciferin in their keto forms.

1keto0   2keto0
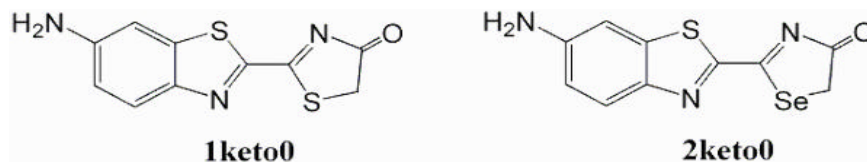
A DFT Study of the Catalytic Mechanism of Ovothiol A

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Histidylcysteine sulfoxide synthetases (OvoA)play a crucial role in the production of redoxdefense molecules for human pathogens andmarine embryos. These non-heme ironenzymes utilize O2 to catalyse their respectivemechanism. In particular, the enzymes use O2to form a cysteine sulfoxide that isnucleophilically attacked by a histidine substrate.Such a process yields the formation of a sulfurcarbon bond between the respective histidine and cysteine producing a histidyl-cysteine sulfoxide. Unfortunately the mechanism by which this operates is not currently known, so it must be elucidated.

Thus, using a DFT custer approach these non-heme iron biochemical systems will be investigated to gain a better understanding in the ways non-heme iron enzymes utilize O2 in their respective mechanisms. Some of the preliminary results will be discussed.

Model of *Campylobacter jejuni* capsular polysaccharide

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Computational modeling of *Campylobacter jejuni* capsular polysaccharide

Theoretical study of the structure of silver clusters by Tabu search in descriptor space

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We studied the silver clusters Ag_n (n=3 20) by tabu search in descriptor space. We did density functional theory calculations with the TPSS functional using the Gaussian G03 software (TPSSTPSS keyword) and a LANL2DZ basis set. For each cluster size, several low energy isomers with different structural descriptors were found. The lowest energy isomer for cluster size (n=3-6) are planar and agree with the earlier theoretical results. For cluster size n>6,we find compact polytetrahedral structures. For $Ag_{16,}$ the lowest energy structure is polytetrahedral as shown . However, Yang et al. in their study, "First-principles study of intermediate size silver clusters: Shape evolution and its impact on cluster properties" using GGA/PBE, predict this structure to be the second lowest energy isomer.
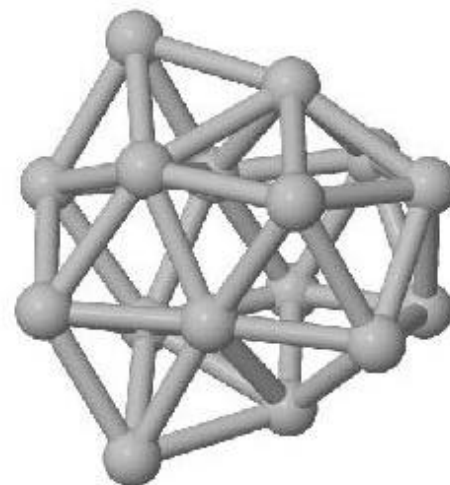
The calculated cohesive energies vary between 0.84eV/atom for Ag_3 and 1.68 eV/atom for $Ag_{16:}$ for comparison, the experimental bulk cohesive energy of silver is 2.95 ev/atom. Our n-atom silver GM have numbers of nearest-neighbour pairs (NN) that are slightly smaller than for Lennard-Jones clusters (NN-LJ). They are as follows in the format (n: NN, NN- LJ) : (3:3,3), (4:5,6),(5:7,9),(6:9,12),(7:16,16),(8:18,18),(10:25,26),(16:42,47).

Identification of Transition States Using MD-Generated Volume Profiles and Volumes of Activation

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The effect of pressure on reaction rates is traditionally expressed in terms of logarithmic pressure derivatives, known as activation volumes. According to transition state theory, activation volumes can be identified as the difference in volume between the transition state (TS) and reactant species:

$$-RT(\partial \ln k/\partial P)_T = \Delta V_{exp} = V_{TS} - V_R.$$

Recently, we proposed a method[1] that uses molecular dynamics (MD) simulations for calculation of accurate theoretical values of activation volumes. This method can be extended for calculation of volumes of any transient structure along reaction coordinate y to produce theoretical reaction volume profile $\Delta V_{MD}(y)$. If the position y_{TS} of the TS along the reaction coordinate is unknown, it can be found from the experimental activation volume ΔV_{exp} by locating it on the MD-generated volume profile: $\Delta V_{MD}(y_{TS}) = \Delta V_{exp}$. In this work we present a test of our methodology for two model systems: isomerization in a bistable diatomic and conformational changes in a long chain with strongly interacting termini. The TS structures determined from the volume profiles were in good agreement with the true TS structures.

[1] H. Wiebe et al, *J. Phys. Chem. C*, 2012, **116**, 22402245; J. Spooner et al, *Phys. Chem. Chem. Phys.*, 2012, **14**, 2264-2277.

Predicting Molecular Properties with Machine Learning

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Determining the properties of molecules has always been one of the major tasks of chemical research. When one is searching for an existing molecule with a desired property, or trying to design a new molecule with a desired property, one often needs to consider thousands of possible compounds. This makes the experimental and computational material property determination of innumerable possibilities costly and impractical in most cases. On the other hand, there are many properties that are not directly measurable experimentally or computable theoretically. For example, one can look at the toxicity of molecules: it would be unethical to test these molecules experimentally, and it is computationally intractable to simulate the ingestion, digestion, and biochemical response of a molecule.

However, by exploring the machine learning methods, we can efficiently, and with controlled errors, estimate the properties of a chemical substance by leveraging the results from previous experiments or accurate calculations. The key insight is that similar molecules tend to have similar properties. So, if the properties of a diverse "reference set" of molecules is known, then one can predict the properties of unknown molecules (the "test set") by determining the relationship between the unknown molecules and the reference molecules. The approach we are developing for molecular similarity is based on kriging, a powerful estimation tool originally used in geostatistics [1]. In this presentation, this method is applied to predict various molecular and material properties.

[1] Wackernagel, H., Multivariate Geostatistics: An introduction with applications. Springer-Verlag: New York, 2003.

Simulation Studies of the Vibrational Dynamics of *para*-Hydrogen Clusters

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This paper discusses the construction and application of reduced-dimensional potential energy surfaces for use in performing simulation of *para*-hydrogen clusters. 'Adiabatic-hindered-rotor' averaging treatment of the angular degrees of freedom is employed. The resulting one-dimensional surface is used in quantum Monte Carlo simulations of *para*-hydrogen clusters of varying sizes. Energetic, and structural properties are computed and compared to previously published results, and vibrational frequency shifts are predicted and compared to available experimental measurements.

Mechanochemistry of Bimolecular Reactions: Quantum Chemical Simulations of 1,3-Dipolar Cycloadditions to Carbon-Carbon Double Bonds

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Chemical reactions usually involve the conversion of reactants to products by overcoming an energetic barrier. Most commonly, this process can be assisted by adding energy through heat, light, or electric current. Another option is to overcome the reaction barrier through application of mechanical work, termed mechanochemistry. This method has received much attention from the scientific community in the last decade. Both theoretical and experimental studies have been performed, demonstrating the ability of mechanochemistry to activate reactions, with a strong focus on unimolecular reactions involving bond-rupture, which is intuitively activated by the application of tensile stress. However, bimolecular reactions, which often involve bond formation as well as rupture, have received much less attention. We seek to change this by undertaking an in-depth study of the mechanochemical activation of the Huisgen reaction, a 1,3-dipolar cycloaddition reaction of a nitrone to a carbon-carbon double bond. We observe that large barrier changes can be induced by applying external force to reactions of this type, and the magnitude of these changes can be controlled by the choice of alkene substrate. By studying the changes induced in the geometry of the substrate, we are able to begin explaining the origins of the barrier reduction effect. In addition, by studying the contributions to the barrier change from mechanical work and the contributions from geometry changes, we discover that steric hindrance to a reaction can play a very significant role in the mechanochemical activation of the reaction.

Potential Energy Surfaces of Reaction Systems at Extreme Pressures

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Both experiment and first principles calculations unequivocally indicate that properties of elements and their compounds undergo a tremendous transformation at ultra-high pressures exceeding 100 GPa due to the fact that the difference between intra- and intermolecular interactions disappears under such conditions. Yet, even at much milder pressures of 5-30 GPa, when molecules still retain their individual identity, their chemical properties and reactivity change dramatically. Although first principles MD is perfectly suitable and, in fact, is being increasingly used to describe these systems, its applications are severely restricted by their size and complexity. We use quantum mechanical and molecular dynamics simulations to show that the high-pressure free energy surfaces $G(x;P)$ (x is a multidimensional geometrical parameter) are well approximated by equation $G(x;P) = G(x;0) + PV(x)$, here $G(x;0)$ is the zero-pressure free energy surface and $V(x)$ is the volume of reaction system in configuration x.

Temporal quantum mechanics / molecular mechanics method for extending the time scales accessible in molecular dynamics simulations of reactions

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An efficient quantum mechanics (QM) / molecular mechanics (MM) method is presented for molecular dynamics (MD) simulations of the reactions that are coupled to time-dependent external driving mechanism. This approach combines three different methods in timely fashion to achieve its efficiency using their positive aspects: quantum chemical (QC) methods to model changes in bonding and electronic structure during reactions, semi-empirical molecular orbital methods to assess the likelihood of trajectories overcoming reaction barriers through short MD simulations, and computationally inexpensive force-fields (FFs) methods to simulate the system the rest of the time. The method introduces a generalized reaction metric to monitor the progress of the simulation in relation to the reactions, and establishes an essential systematic mechanism to switch between FF and QC methods which has a broader implication in QM/MM methods in general.

Interpreting Barium Blockade Kinetics of Potassium Channels using Multi-Ion Potential of Mean Force Calculations

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The mechanism by which ion channels allow the selective yet rapid permeation of K^+ across a cell membrane remains one of most hotly debated questions in biophysics. A high resolution crystal structure of one such channel (KcsA) revealed that selectivity is achieved when ions pass through a narrow selectivity filter formed by a series of backbone amide carbonyls. Ions pass through this filter in a desolvated state, binding in a series of sites (denoted S_0, S_1, S_2, S_3, and S_4), where they coordinate to the filter carbonyls. Miller and coworkers determined that at least one of these sites must be thermodynamically selective for K^+ through experiments where the slowly-permeant Ba^{2+} ion was used to blockade the filter. The external concentration of $K+$ was found to extend the lifetime of these blockades, while the external Na^+ concentration had no effect, indicating that one of the binding sites selectively binds K^+ ions, "locking in" Ba^{2+}. Directly modelling these experiments is an elegant test of computational models and theories of channel selectivity within a thermodynamic framework. We have used novel replica exchange molecular dynamics (REMD) techniques to calculate the potential of mean force (PMF) for the movement of Ba^{2+} from site S_3 to site S_2 and from site S_2 to site S_1. These PMFs indicate that site S_1 is likely the K^+ selective lock-in site. Remarkably, the selectivity of these sites appears to be enhanced by the presence of Ba^{2+} within the filter, as the increased ion-ion electrostatic repulsion pushes the lock-in ions into more K^+ selective regions higher in the sites. This suggest that Ba^{2+} blockade experiments may overestimate the selectivity of the lock in site.

Electron transfer and other reactions in proteins: towards an understanding of the effects of quantum decoherence

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We have embarked on a multistage research program on the multiscale theory, simulation, computation and understanding of electron transfer and other reactions in complex bio-systems. Our entry into the field was our recent tunneling pathway analysis on molecular dynamics simulations of the methylamine dehydrogenase (MADH)amicyanin (Am) redox pair. We found that the most frequently occurring molecular configurations afford superior electronic coupling, via a hydrogen-bonded "water bridge" between donor and acceptor. Mutant complexes fail to achieve bridge stability. A second contribution reports our first attempts to understand the effects of quantum decoherence on the rates of chemical reactions. Multiple-state reaction rates can be estimated within semi-classical approaches provided the hopping probability is taken into account. This probability is intimately related to the transition from the fully quantum to the semi-classical description. Quantum nuclear effects like decoherence and dephasing are not present in the usual rate constant expressions. We included these effects through the introduction of a phenomenological quantum decoherence function. In addition to the electronic coupling term, a characteristic decoherence time tau_dec now also appears as a key parameter. The new formula has been tested by means of DFT molecular dynamics simulations for a triplet to singlet transition within a copper dioxygen adduct and for an electron-transfer model involving a Li donor and a Li+ acceptor, separated by up to five peptide units. We are now setting up to re-examine MADH-Am with this new method, hence avoiding the empiricism of the pathway model.

GKCI Approach to Solving the Electronic Schrödinger Equation

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Few electronic structure methods are able to obtain the accuracy required to predict experiments (less than a milliHartree error). The most obvious method for reliably achieving this accuracy is the full-configuration interaction (Full-CI) method.   However, Full-CI is very computationally expensive (exponential scaling) and as such is rarely useful other than for benchmarking calculations. Full-CI is a method that would work for any arbitrary Hamiltonian. Thus, Full-CI does not take advantage of the inherent smoothness associated with the solutions to the electronic Hamiltonian. Results from Griebel et al.[1] and others[2-4] in the mathematics of complexity literature show that if the analytic solutions to the electronic equation have mixed bound derivatives then it is possible to obtain Full-CI accuracy with polynomial scaling (at least in the large basis set limit). The approach involves selecting a subset of the solutions to the Hartree-Fock equations. The theorems indicate which solutions to include based on the number of nodes in each solution. We refer to this approach as GK-CI.[5] This Full-CI truncation (or multireference CI) does not require any physical intuition of orbitals (the Hartree-Fock solutions) and is not constructed from the typical excitation-hierarchy approach. In this presentation I will explain the method as well as provide preliminary results from both electronic structure and nuclear structure calculations.

1. M. Griebel and S. Knapek, Constr. Approx. 16, 525 (2000)
2. H. Bungartz and M. Griebel, Acta Numer. 13, 147 (2001)
3. G.W. Wasilkowski and H. Wozniakowski, Found. Comput. Math., 5, 240 (2005)
4. S.A. Smolyak, Dokl. Akad. Nauk 4, 240 (1963)

Symmetric two-point weighted density approximation for exchange-correlation energies

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We describe a symmetric, two-point, nonlocal weighted density approximation for the exchange-correlation energy of atoms and molecules and compare it to conventional density functionals and the conventional weighted density approximation. Even the simplest two-point weighted density approximation gives results comparable to the best generalized gradient approximations. Unlike those functionals, however, the two-point weighted density approximation is fully nonlocal, has no self-interaction error, approximately fulfills the Pauli principle, and preserves the uniform electron gas limit.

Water and Aqueous Solutions: New Insights from Large-Scale Computer Simulations

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Water and its anomalies have been the subject of debate for decades. There is now some agreement that the anomalous behaviour of water is in some way related to the presence of two types of local structure: energetically favoured, highly tetrahedral environments, and entropically favoured states with less tetrahedral order. We show explicitly how the presence of these differing local structures can lead to anomalous behaviour in the structure factor and compressibility of water under ambient conditions. Additionally, the physical properties of aqueous solutions of small amphiphilic molecules, such as alcohols, alkoxyalcohols, amines, and others can exhibit unusual behaviour at relatively low concentrations. For such systems, particular features observed in both thermodynamic and spectroscopic measurements are often associated with the possible existence of some sort of species aggregation, characterized by a length scale that exceeds that of a single molecule. Such solutions are sometimes described as microheterogeneous, but the exact nature of the microheterogeneity has remained elusive. We have used large-scale molecular dynamics simulations (up to 64,000 molecules) to investigate aggregation and microheterogeneity in two such systems: 2-butoxyethanol/water, and tert-butyl alcohol/water solutions. The simulations reveal much about the nature of the aggregation and microheterogeneity in these systems. Pitfalls that arise in the modelling and simulation of aggregating systems will also be discussed.