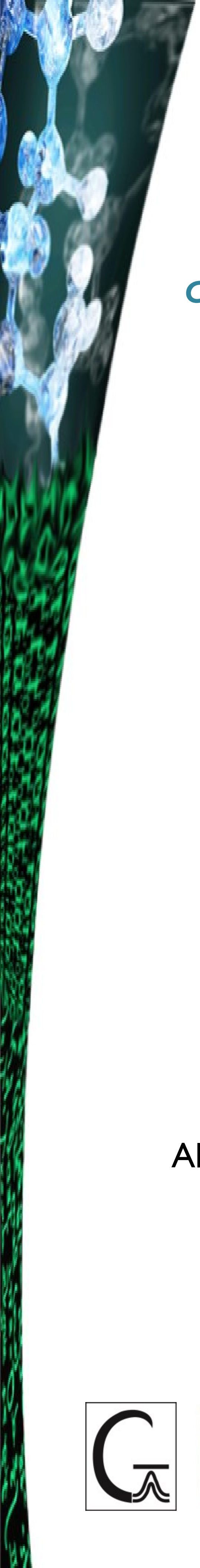


26th CSTCC

Canadian Symposium on Theoretical and Computational Chemistry

Organized by the Canadian Association of Theoretical Chemists (CATC)

July 6 – 11, 2014
Concordia University, Montreal

eBook of Abstracts and Symposium Program

All links within the eBook are highlighted by this shade of **blue**.
Abstract titles link back to the appropriate page
in the Table of contents, and *vice versa*.

CHEMICAL COMPUTING GROUP

Concordia University Arts and Science

Concordia University Research and Graduate Studies

Université de Montréal

Centre for Research in Molecular Modeling CERMM Centre de recherche en modélisation moléculaire

Foreword

Dear CSTCC 2014 Participants,

We are pleased to welcome you to Montreal! The Canadian Symposium on Theoretical and Computational Chemistry (CSTCC) is a merger of two meetings in theoretical and computational chemistry, the oldest of which dates back to 1964. The present edition of the CSTCC is being held at the downtown campus of Concordia University. Besides the numerous new developments in our field that are yours to explore at the meeting, friends and colleagues to meet, discuss and argue with, we hope you find the environment interesting to explore as well. We are happy to have you here and wish you a pleasant and fruitful symposium!

Gilles Peslherbe, Concordia University
Matthias Ernzerhof, Université de Montréal

Acknowledgements

We would like to thank our sponsors, the Centre for Research in Molecular Modeling, the Concordia Office of the Vice-President Research and Graduate Studies, Université de Montréal, the Concordia Faculty of Arts and Science, Gaussian Inc. and the Chemical Computing Group for their generous support, Denise Koch, CERMM Manager, whose role was instrumental in the organization of the symposium, along with Loredana Carbone, Events Coordinator at the Concordia Office of the Vice-President Research and Graduate Studies and Nancy Curran from Hospitality Concordia, as well as the student volunteers Marc-André Bélanger, Soran Jahangiri, Vinodbhai Parmar, Philippe Richer, Philippe Rocheleau, Rodrigo Bohossian Wang, Xi Jun Wang and Yongxi Zhou. Finally, five of our presenting students and post-doctoral fellows will be returning home with a poster prize from the Canadian Association of Theoretical Chemists thanks to the efforts of our colleagues who have volunteered to judge posters, Alex Brown, Tucker Carrington, Mark Casida, Styliani Consta, Robert Doerksen, Allan East, Rene Fournier, Gabriel Hanna, Gerhard Hummer, Peter Kusalik, Branka Ladanyi, Margot Mandy, Sergei Manzhos, Robert Mawhinney, Irina Paci, Pierre-Nicholas Roy, Viktor Staroverov and Qadir Timerghazin. Thank you everyone for helping make this event an enjoyable experience.

Program

Sunday July 6, 2014	Monday July 7, 2014	Tuesday July 8, 2014	Wednesday July 9, 2014	Thursday July 10, 2014	Friday July 11, 2014
	8:00 Registration/Information Conference operations MB 1.301				
	Opening remarks MB 1.201	Registration/Information Conference operations MB 1.301	Registration/Information Conference operations MB 1.301	Registration/Information Conference operations MB 1.301	Registration/Information Conference operations MB 1.301
	Discussion Leader: **Guillaume Lamoureux** **9:00 Benoît Roux** *Structure and energetics of the pumping mechanism of the* Na^+,K^+*-ATPase.*	Discussion Leader: **Marcel Nooijen** **9:00 Troy Van Voorhis** *Using constraints to build active spaces in DFT*	**9:00 CATC Honorary Lecture** Introduction: **Jeremy Schofield** **Raymond Kapral** *Nonadiabatic dynamics in open quantum-classical systems*	Discussion Leader: **Ajit Thakkar** **9:00 Stefan Grimme** *Quantum chemistry for supramolecular complexes*	Discussion Leader: **Russ Boyd** **9:00 Allan East** *Challenges in computing ΔG for reactions in solution*
	9:40 Cecilia Clementi *Multiscale characterization of the photocycle of photoactive yellow protein*	**9:40 Martin Kaupp** *Towards the next generation of local hybrid functionals*	10:00 Coffee break MB 1.245 atrium	**9:40 Weitao Yang** *Exchange-correlation and electronic excitation energies from pairing matrix fluctuations*	**9:40 Carlo Adamo** *Theoretical tools for the design of energy related devices*
	10:20 Coffee break MB 1.245 atrium	10:20 Coffee break MB 1.245 atrium	Discussion Leader: **Dennis Salahub** **10:30 Gerhard Hummer** *Motions in the molecular machinery powering life*	10:20 Coffee break MB 1.245 atrium	10:20 Coffee break MB 1.245 atrium
	Discussion Leader: **Viktor Staroverov** **10:50 Neepa Maitra** *Electron dynamics in strong and weak Fields: Studies of the exact correlation potentials*	Discussion Leader: **Alex Brown** **10:50 Pierre-Nicholas Roy** *Quantum simulations of complex atomic and molecular systems*	**11:10 Dongqing Wei** *Free Energy Calculations of Membrane Systems and CADD*	Discussion Leader: **Natalie Cann** **10:50 Thomas Miller** *Quantum Dynamics from Classical Trajectories: New approaches to simulating biological and molecular catalysts*	Discussion Leader: **Radu Iftimie** **10:50 Peter Kusalik** *Molecular simulations of the crystallization of ice and gas hydrates*
	11:30 Mark Casida *Dressed time-dependent density-functional theory*	**11:30 David Clary** *Combining quantum dynamics and quantum chemistry for reactions of polyatomic molecules*	**11:50 Robert Doerksen** *Computational approaches to cannabinoid receptor drug hit discovery*	**11:30 Berny Schlegel** *Response of molecules to strong laser fields simulated by ab initio molecular dynamics calculations*	**11:30 Branka Ladanyi** *Structure and dynamics of nanoconfined liquids*
	12:10 Lunch LB atrium	12:10 Lunch MB 1.245 atrium (Optional Sitting in LB atrium) and **Poster Session A (A-L)** MB 1.109 atrium	**12:30 Régis Pomès** *Peptides and Proteins in Lipid Bilayers*	12:10 Lunch MB 1.245 atrium (Optional Sitting in LB atrium) and **Poster Session B (M-Z)** MB 1.109 atrium	12:10 Lunch LB atrium
	Discussion Leader: **Mariusz Klobukowski** **13:50 Alexander Wang** *The art of converging the self-consistent field calculations and effective bond-strength indicators*		Free time activity		Discussion Leader: **Erin Johnson** **13:50 Tom Ziegler** *Constricted variational density functional theory. A new DFT approach to the study of excited states*
	14:30 Andreas Goerling *Density-functional methods based on the adiabatic-connection fluctuation-dissipation theorem combining high accuracy and wide applicability*				**14:30 Qadir Timerghazin** *Charge Delocalization in π-Conjugated and π-Stacked Cation Radicals: The Synergy of the Experiment, DFT Calculations, and an Extended Marcus Model*
	15:10 Martin Head-Gordon *Advances in density functional theory calculations for intermolecular interactions*	Discussion Leader: **Irina Paci** **15:10 Mark Ratner** *Structure/function relationships: Organic photovoltaics, perovskites, and extended clusters*		Discussion Leader: **Gabriel Hanna** **15:10 Tucker Carrington** *Calculating vibrational spectra with sum of product basis functions without storing full-dimensional vectors or matrices*	15:10 Coffee break MB 1.245 atrium
	15:50 Coffee break MB 1.245 atrium	**15:50 Hong Guo** *Quantum transport of valley polarized current in 2D transition metal dichalcogenides*		**15:50 Haobin Wang** *Finding the energy eigenstates employing multilayer multiconfiguration time-dependent Hartree theory*	Discussion Leader: **Ray Poirier** **15:40 Guan Hua Chen** *Quantum mechanical simulation of open electronic systems: from molecular devices to graphene*
	Discussion Leader: **Styliani Consta** **16:20 Paul Brumer** *Developments in molecular excitation with natural incoherent light*	16:30 Coffee break MB 1.245 atrium		16:30 CATC Business Meeting MB 1.210	**16:20 Sergei Manzhos** *Search for insertion type anodes for Na and Mg ion batteries based on group IV semiconductors: amorphization, doping, and computational errors*
17:30 Registration EV 11.725	**17:00 Françoise Remacle** *Dynamical studies of ultrafast charge migration in diatomic and modular molecules probed by photoelectron angular distributions*	Discussion Leader: **Dvira Segal** **17:00 Thomas Frauenheim** *DFTB+ - An approximate DFT method: Applications to computational nanomaterials*		17:20 Compute Canada Town Hall Meeting MB 1.210 **Dugan O'Neil**, Compute Canada Chief Science Officer	*Closing remarks* MB 1.201
18:00-20:30 Opening mixer/reception EV 11.725	**17:40 André Bandrauk** *Time-dependent quantum mechanics- with intense ultrashort laser pulses-from Schroedinger to Dirac to Maxwell*	**17:40 Michel Côté** *Many-body effects on the zero-point renormalization of the diamond band structure*			
			19:00 Banquet at Le Windsor		

Symposium venues

- **Opening Mixer/Reception and Registration** (Sunday, July 6, 18:00-20:30): ***#4 on map*** - Engineering, Computer Science and Visual Arts (EV) Complex, room 11.725 (11th floor)

- **Symposium talks**: ***#6 on map*** – Molson Business (MB) Building, room 1.201 (ground floor)

- **Registration/Poster sessions and lunches** (Tuesday, July 8 and Thursday, July 10***): #6 on map*** - Molson Business (MB) Building, ground floor atrium

- **Sit-down lunches** (Monday, July 7 and Friday, July 11): ***#1 on map*** - J.W. Connell Library (LB) Building, ground floor atrium

See the ConcordiaSelfGuidedTour for a full map of the downtown campus

Banquet venue (Wednesday, July 9, 19:00)

Le Windsor

The Windsor Ballrooms
1170, rue Peel, Suite 110
Montréal, Quebec
H3B 4P2

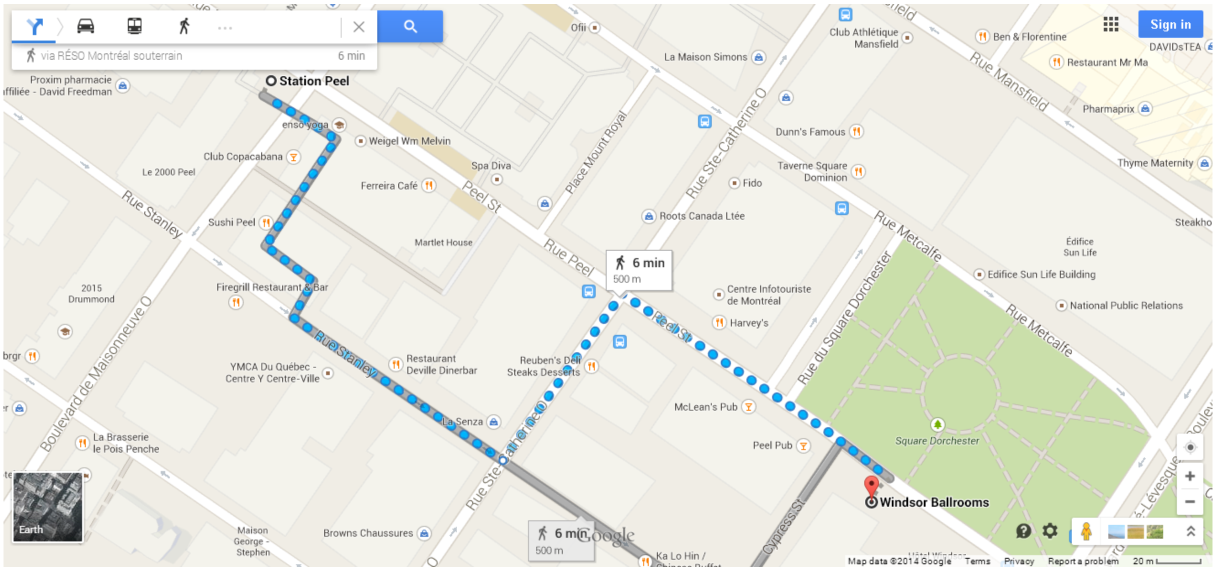


Table of contents

Invited Talks – Monday AM

Invited Talks – Monday PM

Invited Talks – Tuesday AM

Continued…

Table of contents

Invited Talks – Tuesday PM

Invited Talk – Wednesday AM

Invited Talk – Thursday AM

Invited Talk – Thursday PM

Invited Talk – Friday AM

Continued…

Table of contents

Continued…

Table of contents

Continued…

Table of contents

Poster Session B

Continued…

Table of contents

Continued…

Table of contents

Structure and energetics of the pumping mechanism of the Na^+,K^+-ATPase

Benoît Roux and Huan Rui
Biochemistry and Molecular Biology, The University of Chicago

Na^+,K^+-ATPase is ubiquitous to all animal cells. It resides in the plasma membrane and is a major player in keeping the physiological K^+ and Na^+ concentration gradient across the cell membrane in check. It works via a ping-pong mechanism making iterative transitions between the inward-facing (E1) and outward-facing (E2) conformations. The E1 conformation binds three Na^+ from the intracellular side and transports them to the extracellular cell matrix using the energy from ATP hydrolysis. The release of Na^+ and the binding of K^+ at the extracellular side trigger the structural transition to the E2(K2) state, which imports two K^+ into the cell, followed by the turning back to the E1 conformation and the cycle continues. Although the rough scheme of the pumping cycle is known, the transition mechanisms between the conformational states and why a given state preferentially binds K^+ or Na^+, both monovalent cations, is not understood. Using homology modeling and molecular dynamics simulation techniques, this study aims to reveal the conformational changes between all the states in the pumping cycle for the first time. It has successfully produced an outward facing pump structure with two K^+ ions accessible from the extracellular matrix. The current study also explains the origin of the ion binding specificity associated with different conformational states. Furthermore, the gating charges, dissociation constant, and the rate constants of the occlusion/deocclusion processes upon extracellular K^+ binding are calculated and shown to be in excellent agreement with experimental data. The findings of this work are a nice addition to the current understanding of the P-type ATPase pumping cycle and the generated structural models provide basis for future experimental validation.

Multiscale characterization of the photocycle of photoactive yellow protein

Cecilia Clementi
Department of Chemistry, Rice University

The postulated signaling state of the bacterial photoreceptor photoactive yellow protein (PYP) is found in experiments to be essentially indistinguishable from an on-pathway folding intermediate formed upon the isomerization of the chromophore embedded in the protein, suggesting a direct link between the folding and the photocycle of this protein. The wide range of time-scales covered during the photocycle/folding of PYP, together with the partially unfolded nature of the signaling state, make the structure determination of the signaling state challenging, either by simulation or by experiment. We have circumvented this problem by using a realistic coarse-grained protein model for PYP, that allows us to characterize the functional changes in the folding free energy landscape. While the folding landscape of the coarse-grained native protein indicates a two-state folding mechanism, the coarse-grained model of the photoactivated form of PYP populates an on-pathway intermediate ensemble, in line with experimental data. The folding intermediate detected in our coarse-grained study matches well all available experimental data on the putative signaling state of PYP, confirming the connection between the folding and function of this protein. These results allow us to use the coarse-grained model as a starting point to characterize the molecular structure of the signaling state at atomic level of detail.

Electron dynamics in strong and weak fields: Studies of the exact correlation potentials

Neepa T. Maitra
Department of Physics, Hunter College and Graduate Center of the City University of New York

By studying some exactly-solvable models of charge-transfer dynamics and strong-field processes, we find that the exact correlation potential of time-dependent density functional theory develops strongly non-adiabatic and spatially non-local features in time that are missed by the currently available approximations. We analyze these features in terms of kinetic and interaction contributions, and explore orbital-dependent functionals to model them. When the coupling to quantum nuclear dynamics is accounted for, we find additional terms in the potential acting on the electronic subsystem, that fully account for electron-nuclear correlation, and that can yield significant differences to the traditional potentials used when computing coupled electron-ion dynamics.

Dressed time-dependent density-functional theory

Mark E. Casida
Département de Chimie Moléculaire, Université Joseph Fourier (Grenoble I)

Time-dependent (TD) density-functional theory (DFT) provides a theoretical framework for treating the time-dependent response of traditional ground stationary-state DFT to a dynamic perturbation. Electronic excitation spectra may be extracted from the poles of the dynamic polarizability [1]. While TDDFT has become one of the most used methods for studying the excited states of medium and large sized molecules, several difficulties with conventional TDDFT have emerged over the last two decades and are being addressed by various groups [2,3]. We have been concentrating on solving the problem of lack of explicit double excitations in TDDFT [3]. One approach to including double excitations is to do many-body perturbation theory (MBPT) on top of TDDFT in its Green's function formulation and then try to identify the most important correction terms. In this talk, I will summarize the double excitation problem with conventional TDDFT and our experiences with the dressed TDDFT approach [4,5]. An important conclusion is the need to include some exact exchange at the TDDFT level before making MBPT corrections.

[1] M.E. Casida, in *Recent Advances in Density Functional Methods, Part I*, edited by D.P. Chong (Singapore, World Scientific, 1995), 155.
[2] M.E. Casida, *J. Mol. Struct. (Theochem)* **914**, 3 (2009) .
[3] M.E. Casida and M. Huix-Rotllant, *Annu. Rev. Phys. Chem*. **63**, 287 (2012).
[4] M. Huix-Rotllant and M.E. Casida, *cond-mat.mes-hall.* 9 Aug 2010.
[5] M. Huix-Rotllant, A. Ipatov, A. Rubio, and M.E. Casida, *Chem. Phys*. **391**, 120 (2011).

Invited Talk **Monday, July 7** **13:50**

The art of converging the self-consistent field calculations and effective bond-strength indicators

Alexander Wang
Department of Chemistry, University of British Columbia

Based on the corrected Hohenberg-Kohn-Sham energy functional (cHKS) [1], we present several new methods to accelerate self-consistent field (SCF) convergence by utilizing linear-expansion shooting techniques (LIST) [2-4], which outperform Pulay's DIIS [5] and its recent improvements, including EDIIS and ADIIS [6-8].

Here is a chemistry challenge: how to efficiently pinpoint the weakest bond from hundreds or even thousands of them for a given large molecule? Such a perplexing problem is routinely tackled in the mechanistic investigations of chemical reactions and in the design, synthesis, and performance studies of functional materials. If time permits, the second half of this talk will show how to design effective structural indicators to identify weak bonds. Our encouraging results [9] have proven the following strategy to meet the challenge: first using our two new bond-strength indicators to single out a handful potentially weakest bonds and then calculating their bond energies to determine the truly weakest bond.

[1] Y. A. Zhang and Y. A. Wang, *J. Chem. Phys*. **130**, 144116 (2009).
[2] Y. A. Wang, C. Y. Yam, Y. K. Chen, and G.-H. Chen, *J. Chem. Phys*. **134**, 241103 (2011).
[3] Y. K. Chen and Y. A. Wang, *J. Chem. Theory Comput*. **7**, 3045 (2011).
[4] M. A. Garcia Chavez, Y. K. Chen, and Y. A. Wang (unpublished).
[5] P. Pulay, *J. Comput. Chem*. **3**, 556 (1982).
[6] K. N. Kudin, G. E. Scuseria, and E. Cances, *J. Chem. Phys*. **116**, 8255 (2002).
[7] X. Hu and W. Yang, *J. Chem. Phys*. **132**, 054109 (2010).
[8] A. J. Garza and G. E. Scuseria, *J. Chem. Phys*. **137**, 054110 (2012).
[9] G.-X. Wang, Y. S. Chen, Y. K. Chen, and Y. A. Wang (unpublished).

Density-functional methods based on the adiabatic-connection fluctuation-dissipation theorem combining high accuracy and wide applicability

Andreas Görling, Andreas Heßelmann, Patrick Bleiziffer and Daniel Schmidtel
Department of Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg

A new generation of density-functional methods exploiting the adiabatic-connection fluctuation-dissipation (ACFD) theorem is presented. These methods belong to the class of approaches based on orbital-dependent exchange and correlation functionals. The exchange energy and the local multiplicative exchange potential, not to be confused with the nonlocal Hartree-Fock exchange potential, are treated exactly. Functionals for the correlation energy are derived from the adiabatic-connection fluctuation-dissipation theorem via time-dependent density-functional theory. In the latter either the simple Coulomb kernel or the Coulomb kernel plus the full frequency-dependent exact exchange kernel is employed, leading to the correlation energy either in the straightforward direct random phase approximation (dRPA) or in a highly accurate approximation termed exact-exchange ACFD (EXX-ACFD). In self-consistent dRPA and EXX-ACFD methods the correlation potential corresponding to the dRPA or EXX-ACFD correlation energy is obtained via the optimized effective potential method. The new approaches, in particular the EXX-ACFD method, are shown to be highly accurate and, in contrast to traditional density-functional methods, to be well-suited for the treatment of Van-der-Waals interactions or situations characterized by strong correlation.

A. Heßelmann and A. Görling, *Mol. Phys*. **108**, 359 (2010).
A. Heßelmann and A. Görling, *Phys. Rev. Lett*. **106**, 093001 (2011).
A. Heßelmann and A. Görling, *Mol. Phys*. **109**, 2473 (2011).
P. Bleiziffer, A. Heßelmann, and A. Görling, *J. Chem. Phys*. **136**, 134102 (2012).
P. Bleiziffer, A. Heßelmann, and A. Görling, *J. Chem. Phys*. **139**, 084113 (2013).
P. Bleiziffer, A. Heßelmann, C. J. Umrigar, and A. Görling, *Phys. Rev. A* **88**, 042513 (2013).

Advances in density functional theory calculations for intermolecular interactions

Martin Head-Gordon
Department of Chemistry, University of California, Berkeley

Progress in electronic structure calculations depend upon advances in the underlying methods, and also the tools available for analyzing the results of calculations using the resulting methods. In this talk, I shall discuss progress made in my group on both fronts.

With regard to core methodology, I will report on the development of an improved density functional. The design principles for this functional are novel and will be discussed. The final functional is the one that emerges as most transferable from tests of over 10,000 competing functional forms. Quite remarkably, the resulting functional involves substantially fewer empirical parameters (only 10) than many existing alternatives. Due to the design choices together with the training procedure, it outperforms every existing density functional tested for intermolecular interactions. It performs competitively with the best existing functionals for applications to thermochemistry and chemical kinetics. Progress towards assessing the best functionals from tests of much larger numbers of competing functional forms will also be reported if progress permits.

With regard to analyzing electronic structure calculations, I shall discuss an approach to intermolecular energy decomposition analysis (EDA) that my group has been developing to permit interpretation of density functional theory calculations. This EDA allows one to separate so-called “frozen” interactions, induced electrostatic polarization, and dative donor-acceptor interactions. As the EDA is performed variationally, one can also assess the role of these distinct contributions on experimental observables. A variety of examples will be presented to show the usefulness of the approach at present. I shall finish with a discussion of limitations and future challenges.

Developments in molecular excitation with natural incoherent light

Paul W. Brumer
Department of Chemistry, University of Toronto

2D photon echo studies on light harvesting systems have generated considerable interest and controversy regarding the possible role of quantum coherence effects in biological systems. As we have previously shown, such studies rely on the response of molecular systems to pulsed laser excitation, which is dramatically different than the response to natural incoherent light. Significantly, the latter produces mixed stationary states, devoid of time dependent coherences.

After briefly summarizing these results we describe new developments in this area, including the importance of various decoherence time scales and molecular properties for reaching mixed states in natural incoherent light, the role of Agarwal-Fano resonances and spontaneous emission in generating long coherence time scales, and the role of doorway states in the molecular response to light. Examples will be chosen from model systems, isomerization in retinal, radiationless transitions in pyrazine, and Rydberg atoms interacting with the cosmic microwave background. The significance of the results for natural light harvesting systems will be emphasized.

Dynamical studies of ultrafast charge migration in diatomic and modular molecules probed by photoelectron angular distributions

Françoise Remacle
Department of Chemistry, Université de Liège

The recent developments in the generation of optical attopulses suggest that it will soon become experimentally feasible to induce and subsequently directly probe ultrafast charge transfer between the end moieties of the modular molecule. One ultrafast pulse creates a non-stationary state of the neutral or of the cation and a second one ionizes it. Such experiments would allow characterizing a purely electronic time scale, before the coupling to the nuclei takes place. This is a pre Born-Oppenheimer regime where the electronic states are not stationary [1].

We will report on realistic pump probe experiments that monitor the ultrafast electronic dynamics in LiH [2], in the medium size bifunctional molecule PENNA (C10H15N) [3] (Fig.1) and in tetrapeptides [4] using a coupled equation scheme that includes the ionization continua and field effects. We show by modelling a 6 fs IR pump-XUV attosecond pulse train (APT) experiment in LiH that the APT can be used to disentangle the coherent superposition of states built by the IR pump pulse. The APT acts as a frequency filter and only probes the superposition of states with a beating frequency matching the time interval between two XUV attopulses of the train.

Our dynamical simulations demonstrate that inducing and probing charge migration between two moieties of modular systems like PENNA or tetrapeptides is possible using realistic parameters for two ultrashort fs photoionizing pulses, either in a UV-UV or IR-UV scheme. The pump pulse can be tailored to produce a coherent superposition of the electronic states of the cation that differ in their energy and spatial localization of their electron density. The time dependent amplitudes of the states of the superposition means that the state of the cation is not stationary and we show that it is beating between the two ends of the molecule. The beating of the electron density between the two moieties of the modular cation system are reflected in the molecular frame photoelectron angular distributions, computed as a function of the delay between the two pulses. Another robust probe of the charge migration between the two ends of the cation is the anisotropy ionization parameter computed as the normalized difference between the ionization yields at the two moieties. Heatmaps of the anisotropy parameter as a function of the delay time between the two pulses and the kinetic energy of the photoelectron exhibit oscillations that reflect the beating periods of the electron density.

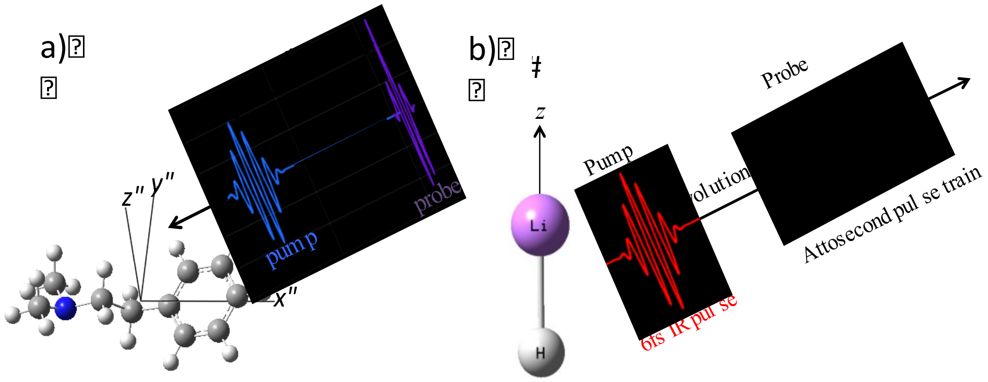
Continued…

[1] F. Remacle and R.D. Levine *An electronic time scale for chemistry,* Proc. Natl. Acad. Sci. USA 103:6793 (2006).

[2] B. Mignolet, R.D. Levine, and F. Remacle, *Phys. Rev. A* **88,** 021403(R) (2014).

[3] B. Mignolet, R.D. Levine, and F. Remacle, *J. Phys. B* (accepted) (2014).

[4] T. Kuś, B. Mignolet, R.D. Levine, and F. Remacle, *J. Phys. Chem. A* **117**, 10513 (2013).



Schematic representation of the pump-probe experiments in (a) PENNA and in (b) LiH.

Time-dependent quantum mechanics -with intense ultrashort laser pulses- from Schrödinger to Dirac to Maxwell

André D. Bandrauk[1] **and Emmanuel Lorin**[2]
[1]Département de chimie, Université de Sherbrooke;
[2]Department of Mathematics-Statistics, Carleton University

Modern laser technology allows for the study of laser-matter interaction in the highly nonlinear nonperturbative regime. Spin-offs of such interactions are the generation of high order harmonic generation, HHG, the current main source of attosecond (10^{-18}s) pulses which are new tools for studying electron dynamics on the electron's natural time scale. Numerical simulations from which appropriate laser-molecule models can be derived require time-dependent algorithms for molecular Schrödinger equations [1] coupled to the photon's Maxwell's equations [2]. Relativistic effects require solutions of time-dependent Dirac-Maxwell equations [3]. Absorbing boundary conditions for high energy electrons on a grid are a ubiquitous problem in high level performance supercomputer simulations. Complex integration time steps are shown to be a useful technique [1] to obtain highly accurate simulations beyond the Born-Oppenheimer regime. Finally, photon momentum, generally neglected in laser-molecule interactions, is shown to undergo unusual partitioning between electrons and nuclei.

[1] A.D. Bandrauk and H.Z. Lu, *J. Theo. Comp. Chem.* **12**, 1340001 (2013).
[2] E. Lorin, S. Chelkowski, abd A.D. Bandrauk, *New J. Phys*. **10**, 025003 (2008).
[3] E. Lorin and A.D. Bandrauk, *Nonlinear Analysis*, **12**, 190 (2012).

Using constraints to build active spaces in DFT

Troy Van Voorhis, Ben Kaduk, David McMahon and Shane Yost
Department of Chemistry, Masschusetts Institute of Technology

One of the outstanding problems in describing low-lying excited states using density functional theory is the importance of static correlation. In wave function methods, this problem is often alleviated by using active space methods: CASSCF, RAS-CI, MCSCF and the like. These methods choose a handful of configurations or orbitals and treat the correlation in this space exactly using CI, thus obtaining a few low lying excited states in a manner that includes static correlation explicitly. Defining an active space in DFT is much harder as there are no orbitals, no configurations and one is implicitly limited to ground state calculations. I will outline some progress that has been made toward doing active space calculations in a DFT framework. Specifically, I will discuss: 1) How constrained DFT can be used to create diabatic states 2) The extent to which non-aufbau occupations of a Kohn-Sham reference are useful at representing locally excited configurations and 3) Methods by which these configurations can be coupled together to form an active space that describes states with multi-reference character. Time permitting, I will discuss some application of these ideas to the problem of singlet fission.

Invited Talk **Tuesday, July 8** **09:40**

Towards the next generation of local hybrid functionals

Martin Kaupp, Alexei V. Arbuznikov, Hilke Bahmann and Toni M. Maier
Institut für Chemie, Technische Universität Berlin

Local hybrid functionals with position-dependent exact-exchange admixture [1], or more generally hyper-GGA-type functionals based on the exact-exchange energy density as crucial ingredient, hold great promise to solve many of the shortcomings of the currently most widely used global hybrid functionals. The fact that local hybrids so far have not yet replaced/superseded global (or also range-separated) hybrids is due to two major obstacles: a) the presence of a local mixing of different exchange-energy densities generates new two-electron integrals that cannot be solved analytically [2]. This has so far rendered local hybrid calculations significantly more computationally demanding than global hybrid treatments. b) The “gauge ambiguity” of local mixing of exact and semi-local exchange energy densities creates fundamental problems that are probably responsible for the fact that so far local hybrids based only on LSDA and exact exchange have provided the numerically best results [3]. In my lecture I will show that significant progress has recently been made on both of these fundamental issues: a) using a semi-numerical integration scheme, we have implemented an efficient Kohn-Sham SCF scheme [4] for local hybrids, as well as a fast semi-numerical TDDFT code [5] into the Turbomole program package. In fact, in combination with an RI-J approximation for Coulomb integrals, the new TDDFT implementation is even faster for large systems than the previous analytical implementation, thus offering now the possibility to evaluate the performance of sophisticated hyper-GGA-type functionals for the excitation spectra of large molecules at no extra cost beyond standard global hybrids. b) We have furthermore recently designed suitable calibration functions to tackle the gauge problem. The first evaluations show that this allows now significantly improved use of GGA exchange-energy densities with exact exchange, opening the way for a new generation of local hybrids with wide applicability [6].

[1] J. Jaramillo, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* **118**, 1068 (2003).
[2] A. V. Arbuznikov, M. Kaupp, and H. Bahmann, *J. Chem. Phys.* **124**, 204102 (2006).
[3] A. V. Arbuznikov and M. Kaupp, *J. Chem. Phys.* **136**, 014111 (2012).
[4] H. Bahmann and M. Kaupp (manuscript in preparation).
[5] T. M. Maier, H. Bahmann, A. V. Arbuznikov, and M. Kaupp (manuscript in preparation).
[6] A. V. Arbuznikov and M. Kaupp (manuscript in preparation).

Quantum simulations of complex atomic and molecular systems

Pierre-Nicholas Roy
Department of Chemistry, University of Waterloo

We will discuss recent advances in path integral simulation methodologies of complex systems with illustrative examples. Both path integral Monte Carlo (PIMC) and path integral molecular dynamics (PIMD) techniques will be considered. Sample applications include the study of energetic, structural, and spectral properties of doped superfluid systems composed of helium and parahydrogen solvent particles. The dopants range from linear molecules to more complex asymmetric tops. New concepts associated with the definition of superfluid response at the nanoscale will be introduced and the conditions for an ideal microscopic probe of superfluid response will be addressed. We will also provide a perspective on the application of these quantum simulation techniques to other interesting nano-confined quantum systems such as water clusters, clathrate hydrates, and molecules encapsulated in fullerenes.

Combining quantum dynamics and quantum chemistry for reactions of polyatomic molecules

David C. Clary
Department of Physical and Theoretical Chemistry, University of Oxford

This lecture will describe research in our group on linking quantum dynamics and quantum chemistry methods to predict the kinetics and dynamics of reactions of polyatomic molecules from first principles. A reduced dimensionality approach is used that combines accurate quantum chemistry calculations of a small number of key points on the potential energy surface with a quantum-dynamical treatment of the bonds being broken and formed in a chemical reaction.

Applications to reactions such as H + cyclopropane, H + butane, CHF_3 and spin-orbit effects in the reaction Cl + CH_4 will be described as will recent computational developments in the method.

The calculations were performed by Xiao Shan, Sarah Remmert, Frank von Horsten and Simon Banks.

Structure/function relationships: Organic photovoltaics, perovskites, and extended clusters

Brett Savoie and Mark Ratner
Department of Chemistry, Northwestern University

The attractiveness of using solar radiation as a fundamental source of electrical power has led to the pursuit of the many different types of photovoltaic capture. We will discuss some that are intrinsically molecular. For the bulk heterojunction type organic photovoltaics, we will discuss the nature of the donor and the acceptor, and how their dynamics can determine the overall behavior. This is extended (in a sketchier way) for the perovskites. Finally, we analyze large clusters of organic molecules, examining their stabilities, their homogeneities, and their connectivity for current passage.

Quantum transport of valley polarized current in 2D transition metal dichalcogenides

Hong Guo
Centre for the Physics of Materials and Department of Physics, McGill University

Recently a large family of 2D monolayer (ML) transition metal dichalcogenides (TMDC) material have been successfully obtained which are stable in ambient conditions. Like graphene, several 2D TMDC have very interesting properties to potentially become electronic materials. Better than graphene, these new 2D materials have direct band gaps larger than 1eV, making them interesting for achieving high on/off current ratio in FET applications.

From the physics point of view, 2D TMDCs such as monolayer WSe_2 have strong spin-orbit interaction. In addition the quantum states in these systems can be well labelled by a valley index τ defined in the reciprocal space and the usual spin index s defined in spin-space. These properties allow both spintronics and valleytronics to be realizable in the same material system. In this talk I shall report atomistic modeling of 2D TMDC materials to qualitatively and quantitatively predict properties of nonequilibrium quantum transport of valley polarized currents. We propose a WSe_2 TMDC transistor to selectively deliver a net valley and spin polarized current $I\tau,s$ to the source or drain of the transistor by circularly polarized light under external bias, paving the way to realize a transport valleytronic system. The generation and delivery of valley polarized electric current is consistent with the optical selection rule reported experimentally.

Collaborators: Kui Gong, Michael Zhang (McGill University), Lei Liu, Eric Zhu (Nanoacademic Technologies Inc.) and Di Xiao (Carnegie Mellon University).

Invited Talk **Tuesday, July 8** **17:00**

DFTB+ - an approximate DFT method: Applications to computational nanomaterials

Thomas Frauenheim
Department of Physics, University of Bremen

The new release of DFTB+ as a density-functional (DFT)-based approach, combining DFT-accuracy and Tight-Binding (TB) efficiency, is reported; http//:www.dftb.org. Methodological details and recent extensions to improve reliability and accuracy will be described briefly. Advanced functions include spin degrees of freedom, time dependent methods for excited state dynamics, and multi-scale QM/MM/Continuum-techniques to treat reactive processes in nanostructures under environmental conditions. Additionally, the combination with non-equilibrium Green´s functions allows to simulate quantum transport in nanostructures and on the molecular scale.

As one latest application chemical vapor deposition (CVD) graphene growth on Cu(111) has been modeled with DFTB molecular dynamics simulations. These simulations demonstrate at the atomic level how high-quality graphene forms on Cu-(111) surfaces. In contrast to other popular catalysts, such as nickel and iron, copper is in a surface molten state throughout the graphene growth at CVD-relevant temperatures supporting 5- and 7-membered ring defects to heal over time.

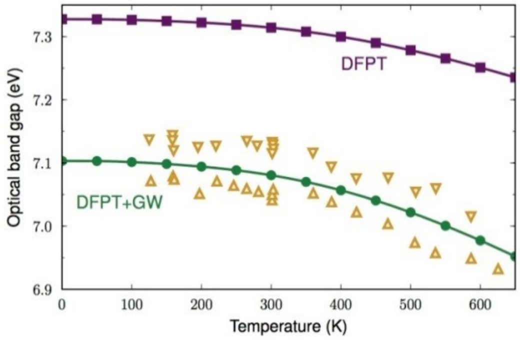
Very recently the time-dependent density functional based tight-binding (TDDFTB) approach is generalized going beyond the Mulliken approach. An additional on-site correction leads to marked qualitative and quantitative improvements over the original method. Especially, the known failure of TDDFTB for the description of $\sigma \rightarrow \pi^*$ and $n \rightarrow \pi^*$ excitations is overcome. Benchmark calculations on a large set of organic molecules also indicate a better description of triplet states. As application we report on excited-state theoretical simulations and experimental studies to investigate the degradation of nitric oxide and acetaldehyde on TiO_2 under VIS and UV irradiation revealing charge transfer complexes on TiO_2 as new source for visible light activity.

Invited Talk **Tuesday, July 8** **17:40**

Many-body effects on the zero-point renormalization of the diamond band structure

Michel Côté[1], Gabriel Antonius[1], Samuel Poncé[2], Paul Boulanger[3] and Xavier Gonze[2]
[1]Département de physique, Université de Montréal;
[2]IMCN-NAPS, Université catholique de Louvain;
[3]Institut Neél

The coupling of electrons to a bosonic field generally causes a renormalization of the energy levels. Whereas in vacuum, the electromagnetic fluctuations lead to the Lamb shift observed in the hydrogen atom levels, in condensed matter, the phonon field renormalizes the band structure, even at zero temperature. Being as large as several hundreds of meV, this renormalization is critical to the predictive power of *ab initio* calculations when it comes to absorption spectra, photovoltaic materials, or topological insulators. Following the early work of Fan and others in the 1950s, the problem was addressed by Allen, Heine and Cardona, whose theory provides perturbative expressions in terms of the electron-phonon coupling. Using semi-empirical methods, and later on, density functional theory (DFT), the temperature dependence of the band gap could be obtained for several semiconductors. Among those, diamond has become a case study where the zero-point renormalization is as much as half an election volt. The reliability of DFT for the electron-phonon coupling has however been challenged in recent years. Since the scattering of an electron by a phonon probes the excited states of a system, a theory describing this process should rely on an accurate unrenormalized band structure, unlike the one of DFT. A truly *ab initio* scheme however would rely on many-body perturbation theory. As such, we have demonstrated previously that such many-body treatment resulted in a significant increase of the electron-phonon coupling in C60 fullerene. In this presentation, I will report on how a careful treatment using many-body perturbation theory as implemented by the GW approach result in an enhancement of the electron-electron interaction causing a 40% enhancement in the zero-point renormalization (ZPR) in diamond with respect to the usual DFT treatment.



Invited Talk **Wednesday, July 9** **09:00**

Nonadiabatic dynamics in open quantum-classical systems

Raymond Kapral
Department of Chemistry, University of Toronto

Quantum processes, such as the electron, proton and coherent energy transfers occurring in biological systems, take place in large complex environments comprising biopolymers and solvent. While the dynamics of a subsystem of the entire system is often of primary interest, its interaction with the remainder of the system, the environment, is responsible for decoherence and other environmental effects. Coupling between the subsystem and environment can lead to the breakdown of the Born-Oppenheimer approximation. The resulting nonadiabatic dynamics plays an important role in many physical phenomena, such as population relaxation following initial preparation of the system in an excited electronic state. The talk will focus on a mixed quantum-classical description of nonadiabatic dynamics and discuss how coherence and decoherence are accounted for in this framework. Methods for simulating the dynamics will be presented and illustrated with calculations of population transfer and coherence for simple models biological and other systems.

Motions in the molecular machinery powering life

Gerhard Hummer
Department of Theoretical Biophysics, Max Planck Institute of Biophysics

Biological molecular machines are highly efficient energy transducers that interconvert chemical, mechanical, electrical, and light energy. We use molecular dynamics simulations and statistical mechanical theory to identify and quantify the molecular mechanisms underlying biological energy conversion processes. Central questions are how simple redox reactions in mitochondria drive the pumping of protons across a membrane against a potential of ~0.2 V; how the resulting electrical and chemical potentials in turn drive the rotary molecular motor ATP synthase; and how this rotation is coupled to the synthesis of ATP from ADP and inorganic phosphate, with ATP being the energy currency of cells. Remarkably, common physical principles emerge in the function of key enzymes involved in energy transduction, including cytochrome c oxidase, complex I, and ATP synthase, despite large variations in their structure and function. In particular, water and hydration effects occupy central roles in the operation of these molecular machines, and are key to achieving both high efficiency and high fidelity in their function.

Invited Talk **Wednesday, July 9** **11:10**

Free Energy Calculations of Membrane Systems and CADD

Dongqing Wei, Yukun Wang, Ruoxu Gu, Huameng Fan, Dan Hu and Jacob Ulmschneider
State Key Laboratory of Microbial Metabolism and College of Life Science and Biotechnology,
Shanghai Jiaotong University

Techniques of rare event dynamics were improved [1] and implemented along with biochemical simulation packages. Charged methyl guanidine is used as a model ion to study the transmembrane permeation of ions. With a widely applied reaction coordinate, our umbrella sampling discovers a dilemma in obtaining the transition trajectory and the potential of mean force — significant finite-size effect in small systems and serious hysteresis in large systems. This suggests the importance of re-examining the validity of the transition trajectory and the potential of mean force obtained in previous works. In this work, a novel reaction coordinate is designed to acquire a continuous trajectory of the permeation process in a large simulation system. This continuous trajectory demonstrates the presence of a water pore at the saddle state which is not clearly observed in previous works. With the presence of the water pore, the energy barrier is shown to be significantly decreased.

Applications were made to study biological systems with relevance to drug design and drug metabolism. The rare event dynamics simulations were performed to understand the kinetic and thermodynamic free energy information on the drug binding sites in the M2 proton channel. Our results give a theoretical framework to interpret and reconcile existing and often conflicting results regarding these two binding sites, thus helping to expand our understanding of M2 drug binding, and may help guide the design and screening of novel drugs to combat the virus [2].

A new agonist of a membrane protein, α7nAChR was discovered with above mentioned simulation technology [3-6], i.e., wgx50, which was tested in vitro experiments that it could combine with α7nAChR on nerve cells, induce depolymerization of Aβ, inhibit Aβ-induced neurocyte apoptosis, and suppress the release of TNF-αand IL-1β from microglia. In vivo experiments showed that it could improve the cognition ability in APP-Transgenic Mice. These results suggest that wgx50 is a promising drug candidate for AD treatment.

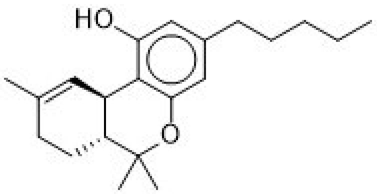
[1] Y. Wang, D. Hu and D.-Q. Wei, *J. Chem. Theory Comput.,* **10 (4),** 1717 (2014).
[2] R.-X. Gu, L. A. Liu and D.-Q. Wei, *J. Am. Chem. Soc.* **133 (28)**, 10817 (2011).
[3] H. R. Arias, R.-X. Gu, D. Feuerbach, B.-B. Guo, Y. Ye, and D.Q. Wei, *Biochemistry*, **50**, 5263 (2011).
[4] P. Lian, D.-Q. Wei, J.-F. Wang, K.-C. Chou, *PLoS ONE*, **6**, e18587 (2011).
[5] H. R. Arias, R.-X. Gu, D. Feuerbach, and D.-Q. Wei, *Biochemistry*, **49**, 4169 (2010).
[6] M. Tang, Z. Wang, Y. Zhou, W. Xu, S. Li, L. Wang, D.-Q. Wei and Z. Qiao, *J. Alzheimer's Disease*, **34**, 203 (2013).

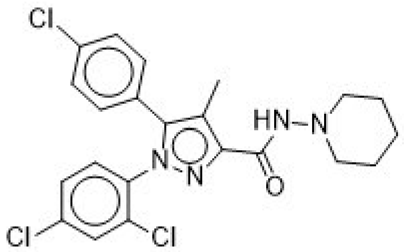
Invited Talk **Wednesday, July 9** **11:50**

Computational approaches to cannabinoid receptor drug hit discovery

Robert J. Doerksen
Department of Biomolecular Sciences, University of Mississippi

The cannabinoid (CB) receptor subtypes 1 and 2 (CB1 and CB2) are class A, G-protein coupled receptors, and represent therapeutically important targets for appetite disorders, as well as for pain management, ischemia, inflammation and cancer. Despite the considerable advancement of X-ray/NMR techniques, there is no available experimental structure of the CB receptors. Hence, we have taken a two-pronged approach to facilitate CB drug discovery. We have utilized ligand-based approaches, including the development and application of machine-learning algorithms, to analyze the requirements for CB receptor binding and activation based on the structures and properties of known CB-active molecules, and for ligand-based virtual screening (LBVS). We also have prepared multiple theoretical CB receptor structure models. We selected the best models and validated them using enrichment studies including docking of known CB ligands from among a large set of decoy compounds. We are using the validated CB receptor models for docking of known ligands to help explain their binding mode and function and for protein structure-based virtual screening (SBVS) or mixed LBVS/SBVS of natural products isolated from traditional psychoactive plants, marine-derived natural products and synthetic compounds. The systematic approaches have led to discovery of novel scaffolds with low nanomolar activity, but more importantly can be generalized to other protein targets. The figure shows prototypical CB ligands, (α)-trans-delta-9-tetrahydrocannabinol (delta-9-THC) (left), a CB1/CB2 agonist and a major psychoactive ingredient of Cannabis sativa, and rimonabant (right), a CB1 inverse agonist.





Peptides and Proteins in Lipid Bilayers

Régis Pomès
Molecular Structure and Function, Hospital for Sick Children
and Department of Biochemistry, University of Toronto

Integral membrane proteins fulfill vital functions involving signalling, recognition, and the exchange of ions and nutrients. Thus, the rapid passage of cations in and out of excitable cells through selective pathways in specialized membrane proteins called ion channels underlies the generation and regulation of electrical signals in all living organisms. Accordingly, the malfunction of membrane proteins is linked to numerous diseases such as cystic fibrosis, and membrane proteins are top targets of drug design efforts. Biological membranes are also the arena in which many battles of bacterial infection and immune response are played out, which may hold clues for the design of new antibiotics.

Despite the importance of these processes to human health and disease, elucidating the molecular mechanisms underlying the interaction of peptides and proteins with lipid membranes has remained challenging. The combination of high-performance computing and efficient sampling algorithms makes it possible to access length- and time-scales relevant to the structure and function of peptides and proteins in lipid bilayers at the atomic level of detail. I will present recent and ongoing molecular simulation studies aimed at characterizing the mechanism of ion transport and selectivity in voltage-gated sodium channels, the kinetics of gating in a magnesium channel, and the interaction of antimicrobial peptides with lipid bilayers.

Quantum chemistry for supramolecular complexes

Stefan Grimme

Mulliken Center for Theoretical Chemistry, Bonn University

Supramolecular complexes are important model systems for understanding non-covalent interactions in biological systems. Due to the size of these host-guest systems (typically a few hundred atoms) and complexity (flexibility, importance of entropy) they represent a challenge for accurate quantum chemical calculations. The talk describes our recent efforts in this field mostly using dispersion corrected density functional theory (DFT-D3).

Approximate coupled-cluster wavefunction based methods (DLPNO-CCSD(T)) and simple MO approaches (DFTB3, HF-3c) are discussed as well. In detail results for the so-called S12L benchmark set of supramolecular complexes are presented. Various problems in the computation of accurate interaction energies and other contributions to the free association energies (e.g. solvation terms, inclusion of counter-ions) are discussed.

Preliminary results for QM/MM based explicit solvation treatments will be presented.

Exchange-correlation and electronic excitation energies from pairing matrix fluctuations

Weitao Yang
Department of Chemistry and Physics, Duke University

We have developed an adiabatic connection to formulate the ground-state exchange-correlation energy in terms of pairing matrix linear fluctuations. This formulation of the exchange-correlation energy opens new a channel for density functional approximations based on the many-body perturbation theory. We illustrate the potential of such approaches with an approximation based on the particle-particle Random Phase Approximation (pp-RPA). This resulting method has many highly desirable properties. It has minimal delocalization error with a nearly linear energy behavior for systems with fractional charges, describes van der Waals interactions similarly and thermodynamic properties significantly better than the conventional RPA, and eliminates static correlation error for single bond systems. Most significantly, it is the first known functional with an explicit and closed-form dependence on the occupied and unoccupied orbitals, which captures the energy derivative discontinuity in strongly correlated systems.

We also adopted pp-RPA and the particle-particle Tamm-Dancoff approximation (pp-TDA) to approximate the pairing matrix fluctuation and then determine excitation energies by the differences of two-electron addition/removal energies. This approach captures all types of interesting excitations: single and double excitations are described accurately, Rydberg excitations are in good agreement with experimental data and CT excitations display correct 1/R dependence. Furthermore, the pp-RPA and the pp-TDA have a computational cost similar to TDDFT and consequently are promising for practical calculations.

To further explore the potential use of pairing matrix dependent functionals, we developed the linear-response time-dependent density-functional theory with pairing fields with both adiabatic and frequency-dependent kernels. The linear-response theory is established based on the representability assumption of the pairing matrix. The linear response theory justifies the use of approximated density functionals in the pp-RPA equation. This work sets the fundamentals for future density-functional development to enhance the description of ground state correlation energies and $N \pm 2$ excitation energies.

J. Cohen, P. Mori-Sanchez, and W. T. Yang. *Chem. Rev.* **112**, 289 (2012).
H. van Aggelen, Y. Yang, and W. T. Yang. *Phys. Rev. A* **88**, 030501(R) (2013).
Y. Yang, H. van Aggelen, S. N. Steinmann, D. Peng, and W. T. Yang. *J. Chem. Phys.* **139**, 174110 (2013).
D. G. Peng, S. N. Steinmann, H. van Aggelen, and W. T. Yang. *J. Chem. Phys.* **139(10),** 104112 (2013).
Y. Yang, H. van Aggelen, and W. T. Yang. *J. Chem. Phys.* **139**, 224105 (2013).
D. G. Peng, H. van Aggelen, Y. Yang, and W. T. Yang. *J. Chem. Phys.* **140**, 18A522 (2014).

Quantum dynamics from classical trajectories: New approaches to simulating biological and molecular catalysts

Thomas F. Miller
Division of Chemistry and Chemical Engineering, California Institute of Technology

A primary focus of our research is the development of dynamics simulation methods that reveal the mechanistic details of quantum mechanical reactions that are central to biological and molecular catalysis. The nature of this effort is three-fold: firstly, we work from the foundation of quantum statistical mechanics and semiclassical dynamics to develop path-integral methods that significantly expand the scope and reliability of condensed-phase quantum dynamics simulations. Secondly, we develop quantum embedding methods that improve the description of molecular interactions in systems with subtle electronic properties. And finally, we apply these methods to the elucidation of genuinely complex systems, including enzyme reactions and inorganic electron-transfer and proton-coupled electron transfer (PCET) processes.

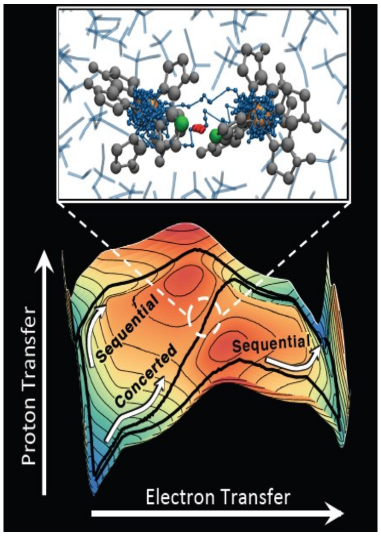
In the talk, we will describe new path-integral methods for the direct simulation of condensed-phase electron transfer, proton transfer, and PCET reactions [1]. Specific topics will include (i) direct simulation PCET reaction mechanisms and rates in iron bi-imidazoline systems across multiple regimes [2,3], and (ii) recent progress in simulation of multi-electron processes [4].

[1] S. Habershon, D.E. Manolopoulo, T.E. Markland, and T.F. Miller, *Annu. Rev. Phys. Chem.*, **64**, 387 (2013).

[2] J.J. Warren, A.R. Menzeleev, J.S. Kretchmer, T.F. Miller, H.B. Gray, and J.M. Mayer, *J. Phys. Chem. Lett.*, **4**, 519 (2013).

[3] J.S. Kretchmer and T.F. Miller, *J. Chem. Phys.*, **138**, 134109 (2013).

[4] A.R. Menzeleev, F. Bell, and T.F. Miller, *J. Chem. Phys.*, **140**, 064103 (2014).



Invited Talk **Thursday, July 10** **11:30**

Response of molecules to strong laser fields simulated by ab initio molecular dynamics calculations

H. Bernhard Schlegel, Wen Li, Suk-Kyoung Lee, Bishnu Thapa and Pascal Krause
Department of Chemistry, Wayne State University

When subjected to short, intense laser pulses, a substantial amount of vibrational energy can be deposited in a molecule. Such highly energized molecules can undergo rapid rearrangements and dissociation. The effect of a strong electric field on the motion of a molecule can be simulated by *ab initio* classical trajectory calculations in the time-varying field. We have examined the fragmentation patterns of methanol cation caused by intense laser pulses. If the molecule can be aligned in the intense laser field, the simulations show selective dissociation of stronger bonds in CF_3Br^+ and $C_6H_5I_2^+$, and enhanced yield of higher energy HCl^+ products in the fragmentation of formyl chloride cation, $ClCHO^+$. A new, more accurate Hessian-based predictor-corrector algorithm for simulating classical trajectories of molecules in intense laser fields will also be discussed.

Calculating vibrational spectra with sum of product basis functions without storing full-dimensional vectors or matrices

Tucker Carrington and Arnaud Leclerc
Chemistry Department, Queen's University

We propose an iterative method for computing vibrational spectra that significantly reduces the memory cost of calculations. It uses a direct product primitive basis, but does not require storing vectors with as many components as there are product basis functions. Wavefunctions are represented in a basis each of whose functions is a sum of products (SOP) and the factorizable structure of the Hamiltonian is exploited. If the factors of the SOP basis functions are properly chosen, wavefunctions are linear combinations of a small number of SOP basis functions. The SOP basis functions are generated using a shifted block power method. The factors are refined with a rank reduction algorithm to cap the number of terms in a SOP basis function. The ideas are tested on a 20-D model Hamiltonian and a realistic CH_3CN (12 dimensional) potential. For the 20-D problem, to use a standard direct product iterative approach one would need to store vectors with about 10^{20} components and would hence require about 10^{12} GB. With the approach of this paper only 1 GB of memory is necessary. Results for CH_3CN agree well with those of a previous calculation on the same potential.

Finding the energy eigenstates employing multilayer multiconfiguration time-dependent Hartree theory

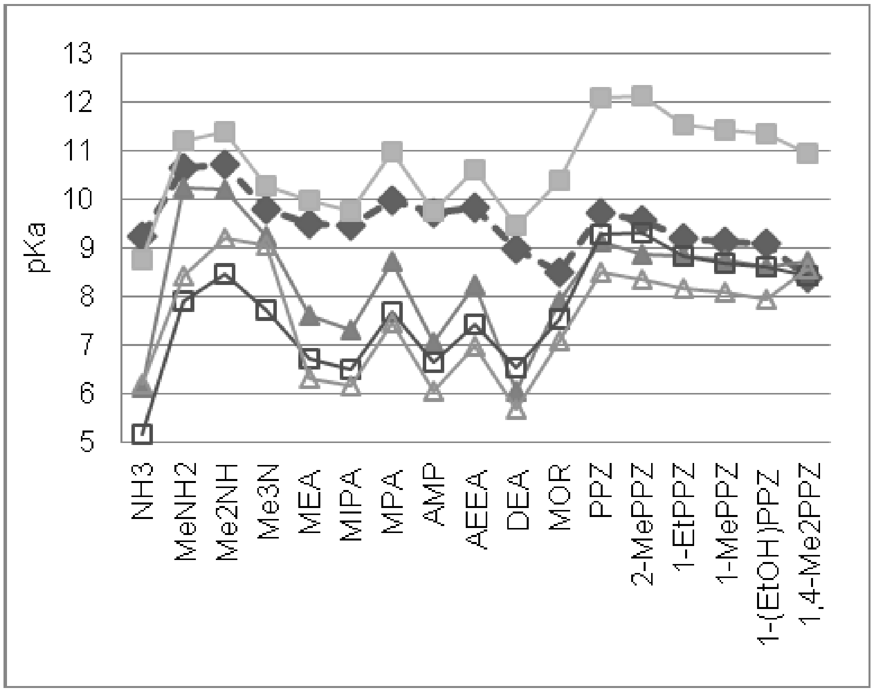
Haobin Wang
Department of Chemistry and Biochemistry, New Mexico State University

The multilayer multi-configuration time-dependent Hartree (ML-MCTDH) theory is a rigorous quantum approach that is based on an efficient representation of the functional in a time-dependent variational calculation. In practice it recursively expands the wave function in several (or many) dynamically contracted layers. One can, however, extends its applicability to the calculation of energy eigenstates, as described in the earlier work of "improved relaxation" by Meyer and co-workers in the context of MCTDH. In this talk we will present a method in this regard, where a Krylov subspace method (Lanczos or Arnoldi) is employed to compute the energy eigenstates iteratively and imaginary-time ML-MCTDH is used as a pre-conditioner. As an application, we discuss the calculation of energy splitting and susceptibility in the spin-boson model and how these can be used to predict the phase transitions in the strong coupling regime.

Challenges in computing ΔG for reactions in solution

Allan L. L. East
Department of Chemistry and Biochemistry, University of Regina

Recently my research group has been trying to improve on prediction of Gibbs (free) energies of reaction (ΔG°) and activation ($\Delta G^{\ddagger}$) in solution, for prediction and comparison of equilibrium constants and rate constants. Two projects are presented: (i) prediction of acid dissociation constants Ka of aqueous amines (for CO_2 capture), and (ii) prediction of equilibrium and rate constants for reactions with solvent participation (for hydroboration of alkenes). In the Ka prediction project, the challenge is in computing solvation free energies for solutes that strongly interact with solvent (RNH_2, RNH_3^+, H^+). In the hydroboration project, the challenges are in incorporating both polarization and entropy damping effects of solvation, and in converting between rate constants and $\Delta G^{\ddagger}$. Limitations of the continuum-solvation approximation in these studies are discussed.



Invited Talk **Friday, July 11** **09:40**

Theoretical tools for the design of energy related devices

Carlo Adamo
Institut de Recherche Chimie Paris, CNRS

Although most of the technologies underpinning renewable energies are (in principle) ready for large-scale implementation, they still require improvement in order to be competitive at both efficiency and economical level with more traditional sources. Design, synthesis, characterization and application of new materials represent a long process often involving several experimental steps each of them requiring significant human and financial resources. Computational materials science can support and speed up this process. Indeed the understanding of microscopic chemical processes at the base of the energy production can provide valuable insights for their improvement. To this end, an effective computational protocol rest on an expert combination of different ingredients. The most important of them include a reliable approach for electronic structure, an effective model for environmental effects and an interpretation scheme able to covert quantum chemical results in simple yet valuable chemical concepts. This philosophy will be illustrated with selected examples concerning the design of functionalized molecules for dye sensitized solar cells (DSSC) and optoelectronics [1-5].

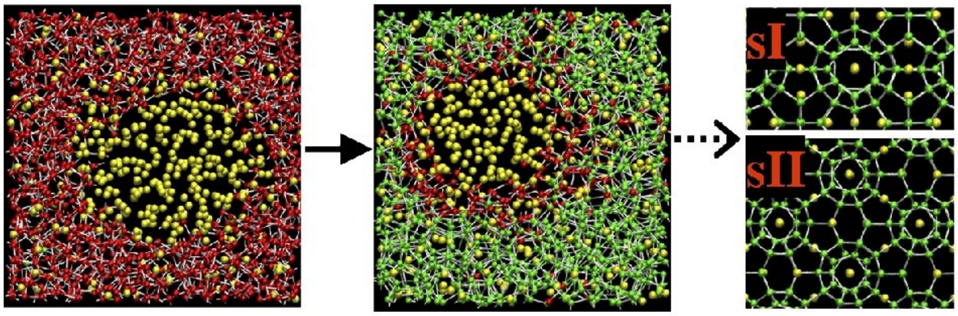
[1] T. Le Bahers, C. Adamo, and I. Ciofini, *J. Chem. Theory Comp*. **7,** 2498 (2011).
[2] F. Labat, T. Le Bahers, I. Ciofini, and C. Adamo, *Acc. Chem. Res*. **45,** 1268 (2012).
[3] I.Ciofini, T. Le Bahers, C. Adamo, F. Odobel, and D. Jacquemin, *J. Phys. Chem. C* **116,** 11946 (2012).
[4] G. Garcia, I. Ciofini, M. Fernández-Gómez, and C. Adamo. *J. Phys. Chem. Lett*. **4,** 1239 (2013).
[5] T. Le Bahers, T. Pauporté, P.P. Lainé, F. Labat, C. Adamo, and I. Ciofini, *J. Phys. Chem. Lett.* 4, 1044 (2013).

Invited Talk **Friday, July 11** **10:50**

Molecular simulations of the crystallization of ice and gas hydrates

Peter G. Kusalik
Department of Chemistry, University of Calgary

While the molecular behaviour within liquids, and water specifically, has been extensively studied, one important aspect of these systems that has remained poorly understood at the molecular level is first order phase transitions of liquids to solids. As a key example of such transitions, the nucleation and growth of ice crystals has numerous implications, notably in atmospheric science. Since few experiments are able to probe directly the microscopic environment of a crystal during its nucleation or the interface of a growing crystal, molecular simulations have afforded us an excellent opportunity to begin to investigate crystal nucleation and growth at a molecular level. In this presentation I will begin with a brief review of some key issues around simulations of crystallization, considering the attributes and limitation of various models and methods. I will describe some approaches we have developed and utilized for the simulation of the formation and growth of crystals, both in the homogeneous and heterogeneous contexts. While specific results for ice will be one focus, the “simpler” case of gas clathrate hydrates will also be examined extensively. These results will demonstrate that the process of crystallization is characterized by collective phenomena involving many molecules, where the organization can be seen to occur in stages. The nature of the structural topology and fluctuations that characterize a solid/liquid interface will be examined and I will show that defects can play key roles in observed behaviours. I will also review recent results that explore the roles of surfaces on nucleation and growth. Through the lens of our current understanding, I will conclude with an exploration of possible future lines of investigation.



Structure and dynamics of nanoconfined liquids

Branka M. Ladanyi
Department of Chemistry, Colorado State University

This presentation will focus on our molecular simulation results for the structure and dynamics of liquids confined in approximately cylindrical pores with diameters ranging from 20 to 40 Å. Most of our work deals with porous amorphous silica, resembling MCM-41 materials, and with water and acetonitrile confined in them. Other model pores are also investigated in order to determine the effects of surface roughness and wettability. We use Gibbs ensemble Monte Carlo simulation to prepare filled pores in equilibrium with bulk fluid and then molecular dynamics simulation to calculate the structure and dynamics of the confined liquid. Our initial characterization of liquid dynamics included translational mean squared displacements, orientational time correlations, and survival probabilities in interfacial shells [1,2]. We found that the radial-axial anisotropy in translational motion largely follows the predictions of a model of free diffusion in a cylinder. However, both translational and rotational molecular mobilities are strongly dependent on the proximity to the interface, with pronounced slowdown in layers near the interface. In order to make contact with experiments on liquid dynamics within the pores, we have calculated and analyzed the self-intermediate scattering function of molecular hydrogens [3], the observable in quasi-elastic neutron scattering (QENS) and the collective polarizability anisotropy time correlation [2], measured in optical Kerr effect (OKE) experiments. Our findings on the dynamics of confined liquids detectable by QENS and OKE will be discussed.

[1] A.A. Milischuk and B.M. Ladanyi, *J. Chem. Phys.* **135**, 174709 (2011).
[2] A.A. Milischuk and B.M. Ladanyi, *J. Phys. Chem. B* **117**, 15729-15740 (2013).
[3] A.A. Milischuk, V. Krewald, and B.M. Ladanyi, *J. Chem. Phys*. **136**, 224704 (2012).

Invited Talk **Friday, July 11** **13:50**

Constricted variational density functional theory. A new DFT approach to the study of excited states

Tom Ziegler
Department of Chemistry, University of Calgary

In the constricted variational density functional theory [1], CV(n)-DFT, we construct excited state KS-orbitals by performing a unitary transformation [2] among occupied $\{\psi_{i;}\ i=1,occ\}$ and virtual $\{\psi_{a;}\ a=1,vir\}$ ground state orbitals

$$Y\begin{pmatrix} \psi_{occ} \\ \psi_{vir} \end{pmatrix} = e^{U}\begin{pmatrix} \psi_{occ} \\ \psi_{vir} \end{pmatrix} = \left(\sum_{m=0}^{\infty}\frac{U^m}{m!}\right)\begin{pmatrix} \psi_{occ} \\ \psi_{vir} \end{pmatrix} = \begin{pmatrix} \psi'_{occ} \\ \psi'_{vir} \end{pmatrix}$$

to order m=n in U. Here ψ_{occ} and ψ_{vir} are concatenated column vectors containing the sets of occupied and virtual ground state (reference) KS-orbitals. The resulting ψ'_{occ} and ψ'_{vir} are concatenated column vectors which contain the sets $\{\psi'_{i;}\ i=1,occ\}$ and $\{\psi'_{a;}\ a=1,vir\}$ of occupied and virtual excited state orbitals, respectively. Further, U_{ai} are the variational mixing matrix elements that combine virtual and occupied ground state (reference) orbitals in the excited state.

To second order (m=2), excitation energies obtained from the variational approach are equivalent to those from time-dependent density functional theory [1]. However, to higher order, the new approach affords a qualitatively correct picture of charge transfer [3] and Rydberg transitions, even with regular GGA functionals. The approach is further kindred to the ΔSCF-DFT procedures predating TDDFT and we describe how adiabatic TDDFT and ΔSCF-DFT are related through different approximations to SCF-CV(n)-DFT. We present application of SCF-CV(n)-DFT[5] to charge, Rydberg , $n \rightarrow \pi^*$ [4] and $\pi \rightarrow \pi^*$ transitions [5] and catalytic systems.

[1] T. Ziegler, M. Seth, M. Krykonov, J.J. Autschbach, and F. Wang, *J. Chem. Phys*. **130**, 154102 (2009).
[2] J. Cullen, M. Krykunov, and T. Ziegler, *Chem. Phys*. **391**, 11 (2011).
[3] T. Ziegler and M. Krykunov, *J.Chem.Phys*. **133**, 74104 (2010).
[4] T. Ziegler, M. Krykunov, and J.Cullen, *J.Chem.Phys*. **136**, 124107 (2012).
[5] M. Krykunov, S. Grimme, and T. Ziegler, *J. Chem. Theory Comput*. **8 (11)**, 4434–4440 (2012).
[6] M. Krykunov and T. Ziegler, *J. Chem. Theory Comput.* **9**, 2761(2013).

Charge delocalization in π-conjugated and π-stacked cation radicals: The synergy of the experiment, DFT calculations, and an extended Marcus model

Qadir K. Timerghazin, Marat R. Talipov and Rajendra Rathore
Department of Chemistry, Marquette University

Aromatic molecules and polymers with extended π-conjugation and/or π-stacking can accommodate and conduct a negative (electron) or a positive (hole) charge, an ability that holds a great promise for developments in photovoltaics and molecular electronics. Further progress in these applications requires a detailed theoretical understanding of the properties of the corresponding anion and cation radicals. The size and the delocalized, open-shell nature of these anion and cation radicals present significant challenges for both experimental studies as well as the electronic structure calculations. Hence, the extent and origins of the trends observed for these systems are still poorly understood, which includes a commonly observed linear 1/n evolution of their redox and optoelectronic properties, where n is the number of monomer units.

This talk will overview our on-going effort in using computational/theoretical approaches to supplement and rationalize the experimental data on the properties of extended π-conjugated and π-stacked cation radicals. We will discuss the challenges and strategies of the DFT studies of extended aromatic cation radicals, and demonstrate that a carefully benchmarked/calibrated DFT approach not only successfully captures the experimental 1/n trends, but also predicts their breakdown–the predictions subsequently verified by the experiment. We will further rationalize these 1/n trends and their breakdown using an elegant multi-center extension of the classical Marcus two-parabola model that faithfully reproduced the experimentally and computationally observed trends with just a few adjusted parameters. Finally, we will discuss the relation of this multi-center model with the classical Hückel theory description of π-systems and the implications of these insights to the design of aromatic molecules with tailored redox and optoelectronic properties.

Quantum mechanical simulation of open electronic systems: From molecular devices to graphene

Guan Hua Chen
Department of Chemistry, University of Hong Kong

In an open electronic system, the number of electrons is not conserved and often fractional, and thus, traditional quantum chemistry methods are no longer applicable. Based on the holographic electronic density theorem, we proposed and developed a first-principles method to simulate the dynamics of open electronic systems [1,2]. A Liouville-von Neumann equation for reduced single-electron density matrix, coupled with Poisson equation, is numerically integrated in the time domain to simulate electronic dynamics of open systems. Transient currents through molecular transistor, carbon nanotube, graphene and molecular wires are simulated and studied [3-6].

[1] X. Zheng, F. Wang, C.Y. Yam, Y. Mo, and G.H. Chen, *Phys. Rev. B* **75** 195127 (2007).
[2] X. Zheng, G. H. Chen, Y. Mo, S. K. Koo, H. Tian, C. Y. Yam, and Y. J. Yan, *J. Chem. Phys.* **133**, 114101 (2010).
[3] C.Y. Yam, Y. Mo, F. Wang, X.B. Li, G.H. Chen, X. Zheng, Y. Matsuda, J. Tahir-Kheli, and W.A. Goddard III, *Nanotech*. **19**, 495203 (2008).
[4] R. Wang, D. Hou and X. Zheng, *Phys. Rev. B* **88**, 205126 (2013).
[5] Shuguang Chen, Hang Xie, Yu Zhang, Xiaodong Cui, and G.H. Chen *Nanoscale* **5**, 169 (2013)
[6] Shuguang Chen, Yu Zhang, SiuKong Koo, Heng Tian, ChiYung Yam, G.H. Chen, and M. Ratner, *J. Phys. Chem. Lett.,* **5**, 1272 (2014).

Search for insertion type anodes for Na and Mg ion batteries based on group IV semiconductors: amorphization, doping, and computational errors

Sergei Manzhos, Fleur Legrain and Oleksandr Malyi
Department of Mechanical Engineering, National University of Singapore

The development of high capacity, high rate post-lithium (Na, Mg) ion batteries is a way towards wider use of renewable electricity. To this end, design of electrode materials with suitable storage energetics and diffusion properties is necessary. We focus on the search of efficient anode materials, which are still lacking. Our own and other labs' studies have shown that insertion of Na, Mg in some materials with great performance for Li ion batteries (such as crystalline Si) is often not favored thermodynamically and hindered kinetically [1-3]. On the other hand, other materials with similar chemical properties might work for Li and Na or Mg, for example, Sn [4].

At the same time, the (dis)charging of an electrode may cut across the phase diagram. Phases' both crystalline and amorphous - which are not thermodynamically most stable for the uncharged electrode at normal conditions may be stabilized by metal ion insertion or external conditions. We summarize our recent comparative computational studies of Li, Na, and Mg insertion into crystalline and amorphous (a-) Si and Sn. We find that amorphous phases may be beneficial for Na and Mg storage in materials where storage in the most stable phase is inhibited. A number of insertion sites were identified in a-Si where the defect formation energy for Li, Na and Mg is below that in diamond Si and is negative (favored insertion), while it is positive for diamond Si [5]. The defect formation energy of Na in a-Si is competitive with Na's cohesive energy. We also find that Al doping can also be used to strengthen binding of metal ions with the Si host and that Al-doped Si might work as anode for Na and Mg ion batteries.

For Sn, experiments reported formation and even dominance of the alpha phase upon charge-discharge [6], even though beta-Sn is the more stable phase under normal conditions. We compute relative storage energetics of Li, Na, and Mg in alpha- and beta-Sn and find that beta-Sn does not thermodynamically favor insertion while alpha-Sn does (for Li and Na). We also find wide variability among different DFT setups typically used in the literature, including qualitative differences, which emphasizes that more accurate electronic structure approaches are desirable.

Continued….

[1] O. I. Malyi, T. L. Tan, and S. Manzhos, *App. Phys. Express* **6,** 027301 (2013); *J. Power Sources*, **33,** 341 (2013); *Nano Energy* **2,** 1149 (2013).

[2] T. L. Tan, O. I. Malyi, F. Legrain, and S. Manzhos, *MRS Proc*. **1541** (2013)

[3] F. Legrain, O. Malyi, and S. Manzhos*, Solid State Ionics* **253,** 157 (2013).

[4] N. Singh, T. S. Arthur, C. Ling, M. Matsui and F. Mizuno, *Chem. Commun*. **49,** 149 (2013); L. D. Ellis, P. P. Ferguson and M. N. Obrovac, *J. Electrochem. Soc*. **160,** A869 (2013).

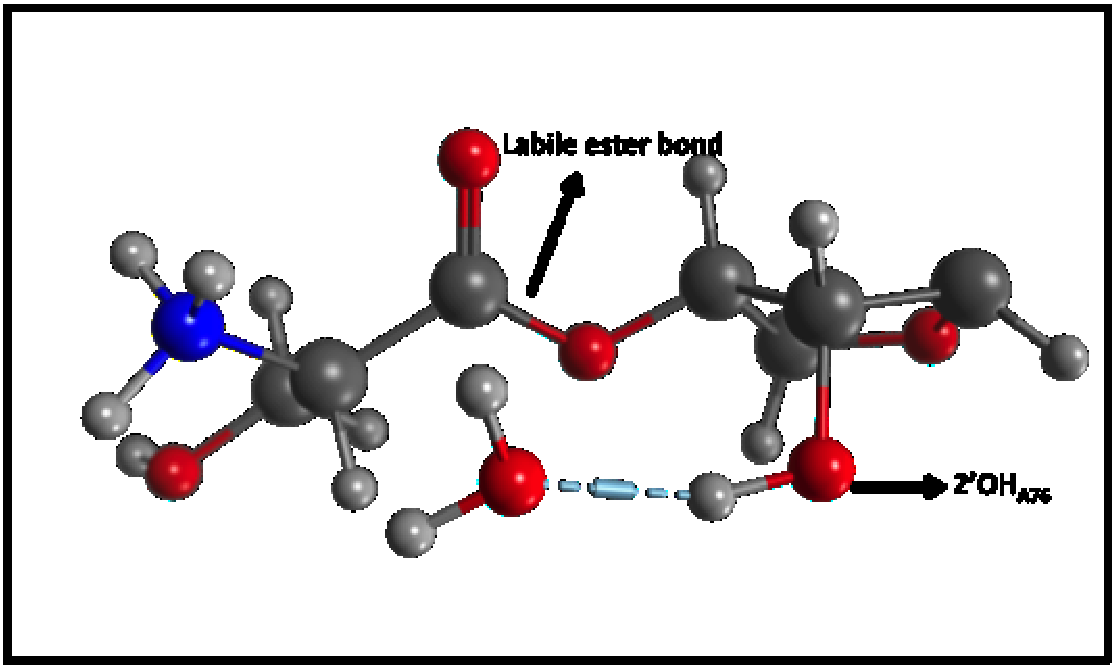
[5] F. Legrain, O. I. Malyi, T. L. Tan, and S. Manzhos, *MRS Proc*. **1540** (2013); F. Legrain, O. Malyi, and S. *Manzhos, Comput. Mater. Sci*. (2014), in print.

[6] K. Hirai, T. Ichitsubo, T. Uda, A. Miyazaki, S. Yagi and E. Matsubara, *Acta Materialia* **56,** 1539 (2008); H. S. Im, Y. J. Cho, Y. R. Lim, C. S. Jung, D. M. Jang, J. Park, F. Shojaei and H. S. Kang, *ACS Nano* **7,** 11103 (2013).

Novel ribozymal catalytic mechanism within ThrRS post-transfer editing function

Mohamed M. Aboelnga and James W. Gauld
Department of Chemistry & Biochemistry, University of Windsor

It becomes problematic for the catalytic site of Threonyl-tRNA (ThrRS) to discriminate its cognate Threonine (Thr) from the structurally related Serine (Ser). In fact, this will result in a misacylated Ser-tRNAThr. Interestingly, in order to overcome this lack of accuracy and to ensure faithful translation, ThrRS appears to act as a double-sieve. In particular, there is a second active site known as an "editing region" where the mischarged tRNA can be cleared by a hydrolytic proofreading mechanism. In this mechanism, the 2'OHA76 of the substrate promotes the reaction by aligning a H_2O molecule in close proximity to the scissile Ser-tRNA ester bond. More interestingly, due to the lack of direct involvement of protein side chains in a way that could facilitate the catalysis, experimentalists suggested that this 2'OH is the only base in the vicinity of this labile bond. Meanwhile, the precise role played by this OH is still a matter of debate. Within our calculation we performed an intensive study utilizing a variety of possible mechanisms by applying MD and ONIOM(QM/MM) methods. Our results suggest that the 2'OH may play a critical role in the editing mechanism.



Selected configuration interaction with truncation energy error in molecular systems: Water ground state energy and bond dissociation in small molecules

Cesar X. Almora-Diaz and Carlos F. Bunge
Theoretical Physics, Universidad Nacional Autonoma de Mexico

A priori selected configuration interaction (SCI) with truncation energy error (SCI-TE) [1] and CI by parts (CIBP)[2] for molecular systems has been implemented in our programs ATMOL y AUTOCL for electronic structure of stationary states [3]. Altogether, SCI-TE and CIBP allow: a) the construction of a model space that contains the principal configurations, b) to calculate the energy truncation error from discarded configurations. In this way, we are allowed to obtain numerical solutions of the Schrödinger equation with controlled and hence predictive accuracy, which is one of the aims of electronic structure theory [4].

In order to test the method we reproduce double zeta basis sets truncated CI and FCI results for water at equilibrium geometry and at geometries where the bond lengths are elongated until dissociation [5, 6]. In all cases, we reproduce exact CI results (from CISD to FCI) to within 10 microhartree, also, we found that energy differences between FCI and $CISDTQQ_nS_x$ results differ in less than 100 microhartree.

At the equilibrium geometry, SCI-TE and CIBP were used to approximate the total nonrelativistic electronic ground state energy with CI up to sextuple excitations. Correlation-consistent polarized core-valence basis sets up to sextuple zeta were employed. Truncation energy errors range between less than 1 μH, and 100 μH for the largest orbital set. Our best upper bound, -76.4343 Hartree, obtained by SCI with up to sextuple excitations with a cc-pCV6Z basis recovers more than 98.8% of the correlation energy of the system, and it is only about 3 kcal/mol above the "experimental" value.

Also, we carried out up to $CISDTQQ_nS_x$ calculations that simulate single, double and triple bond dissociation processes on C_2H_6, F_2, C_2, O_2 and N_2 and compared our results with those of other high-level electronic structure methods.

[1] C.F. Bunge, *J. Chem. Phys.* **125**, 014107 (2006).
[2] C.F. Bunge and R. Carbo-Dorca, *J. Chem. Phys.***125**, 014108 (2006).
[3] C.X. Almora-Diaz, *J. Chem. Phys.* **140**, 184302 (2014).
[4] T. Shiozaki, M. Kamiya, S. Hirata, and E.F. Valeev, *J. Chem. Phys.* **130**, 054101 (2009).
[5] G.K-L. Chan and M Head-Gordon, *J. Chem. Phys.* **118**, 8551 (2003).
[6] J. Olsen, P. Jorgensen, H. Koch, A. Balkova, and R.J. Bartlett, *J. Chem. Phys.* **104**, 8007 (1996).

Boys' collocation method using sparse grids combined with the LSE method to solve the electronic Schrödinger equation

James S. M. Anderson[1], **Hiroyuki Nakashima**[2], **Hiroshi Nakatsuji**[2] **and Paul W. Ayers**[3]
[1]Condensed Matter and Physics Laboratory, RIKEN;
[2]Quantum Chemistry Research Institute, Quantum Chemistry Research Institute;
[3]Chemistry and Chemical Biology, McMasters University

The local Schrödinger equation (LSE) method is a very accurate method for solving the electronic Schrödinger equation. It relies on creating an analytic basis set through iteratively applying the Hamiltonian on some initial basis function. The coefficients of these functions are then determined by solving the electronic Schrödinger equation at a set of points. The LSE method does not have the computational limitation of requiring that the basis be analytically integrable, but finds the best solution that satisfies the equations at each point. Using Boys' theorem the LSE method can be reformulated as a numerical integration problem, i.e. the points can be viewed as numerical integration where the points have uniform weight. Using the Monte-Carlo method to choose the points provides satisfactory results, however the Monte-Carlo method does not take into account the smoothness of the integrand. Relatively recent results from Griebel and others in the mathematics of complexity literature show how one may construct accurate grids for performing efficient numerical integration where the number of points only increase polynomially with respect to dimension. In this presentation the mechanics of the approach will be explained and preliminary results will be shown

Various modes of transition state complexation of t-butyl methyl ketone in its enantioselective reduction

Philippe Archambault and Heidi M. Muchall
Department of Chemistry and Biochemistry, Concordia University

The facial selectivity of prochiral ketones remains a largely unexplored topic in computational chemistry. Although considering the ratios of various activation energies for the transition states is certainly necessary, it is not sufficient for predicting the outcome of enantioselective reactions. Rather, it is crucial to understand which interactions lead to differentiation between the energies of transition states that result in opposite configuration. Our study employs electronic structure theory (DFT level) to investigate the cause of the experimentally established [1] enantioselectivity in the reduction of prochiral ketones with borane catalyzed by a chiral oxazaborolidine. Although computational methods have provided some insight into this reduction [2], the underlying mechanism of facial selectivity remains poorly understood.

The reduction relies upon the catalyst-borane complex approaching the prochiral ketone from the preferred face. Since the hydride transfer is the rate-limiting step, it becomes critical to establish all reasonable ketone orientations within the complex. The often-assumed [1] B···O=C complexation is in fact disfavoured by the reduced electron demand of the catalytic framework's boron atom and therefore leads to only one particular set of plausible ketone orientations. As a first step in this investigation, we present the various modes of complexation of t-butyl methyl ketone and the resulting transition states for hydride transfer.

[1] E.J. Corey and C.J. Helal. *Angew.Chem. Int. Ed*. **37**, 1986 (1998).
[2] G. Alagona, C. Ghio, M. Persico, and S. Tomasi. *J. Am. Chem. Soc*. **125**, 10027 (2003).

Using high-dimensional Smolyak interpolation to solve the Schrödinger equation and represent potentials

Gustavo Avila-Blanco and Tucker Carrington
Department of Chemistry, Queen's University

The most straightforward methods for solving the (ro-)vibrational Schrödinger equation and interpolating or fitting potential energy surfaces (PESs) use product grids and product basis sets. Their size scales as n^D where n is a representative number of functions or points for a single coordinate and D is the dimensionality. Because n is typically about 10, the memory required for such calculations is roughly 8000 GB when D=12. The memory cost grows exponentially with D. Mathematicians call this the "curse of dimensionality". When wavefunctions and PESs are smooth, it is possible to reduce the number of functions and points by orders of magnitude by using Smolyak or sparse grid ideas and to avoid exponential scaling. This attenuates the curse. We apply a new Smolyak-inspired collocation method to compute vibrational energy levels of HONO using bond coordinates. We show that, despite the reduction in the size of the basis and grid, it is possible to exploit product structure to evaluate matrix-vector products efficiently. We had previously used similar ideas only with normal coordinates. It is important to demonstrate that they are useful when used with coordinates better suited to describing large amplitude motion. Closely related ideas are used to interpolate the HONO PES.

Efficient semi-numerical implementation of local hybrid density functionals

Hilke Bahmann
Chemistry, Technische Universität Berlin

In the quest for improved density functionals that can be used for a wide range of properties and systems, local hybrid functionals are promising candidates. They perform well for atomization energies and reaction barriers [1,2] and can be, similarly to any global hybrid functional, augmented with dispersion correction [3] to account for weak interactions. A key quantity in the local hybrid scheme is the exact exchange energy density. For their initial implementation the exact exchange potential (and thus the exact exchange energy density) is expanded in the atomic orbital basis giving rise to a resolution of the identity (RI). While this yields a formal efficiency that is comparable to a global hybrid calculation, the RI-approximation leads to a great demand on the atomic orbital basis rendering this approach unpractical for large applications.

Recently, the efficiency of a semi-numerical implementation of exact exchange in global hybrid functionals has been promoted [4]. In the same context preliminary post-SCF results for local hybrids have been reported [5]. Based on these developments, a semi-numerical self-consistent implementation for local hybrid functionals is presented. The exact exchange energy density and related quantities are evaluated on the same grids that are used for semi-local density functionals. To this end, at each grid point one-electron Coulomb integrals are evaluated analytically and subsequently contracted with the density matrix and basis functions. The formal scaling of this local hybrid implementation is equivalent to global hybrid functionals and there are no special demands on the atomic basis set or the grid size. This implementation enables, therefore, the application of local hybrid density functionals to a large variety of chemically interesting systems. It can be straightforwardly extended to molecular gradients and TDDFT.

[1] H. Bahmann, A. Rodenberg, A. V. Arbuznikov, and M. Kaupp, *J. Chem. Phys*. **126**, 011103 (2007).
[2] M. Kaupp, H. Bahmann, and A. V. Arbuznikov, *J. Chem. Phys*. **127**, 194102 (2007).
[3] K. Theilacker, A. V. Arbuznikov, H. Bahmann, and M. Kaupp, *J. Phys. Chem. A* **115**, 8990 (2011).
[4] F. Neese, F. Wennmohs, A. Hansen, and U. Becker, *Chem. Phys*. **356**, 98 (2009).
[5] P. Plessow and F. Weigend, *Comp. Chem*. **33**, 810 (2012).

Quantum free energy calculations on the water dimer

Kevin P. Bishop and Pierre-Nicholas Roy
Department of Chemistry, University of Waterloo

Free energy calculations of chemical systems are some of the most expensive computations to perform. Techniques such as umbrella sampling have improved the accuracy of the free energy calculated but have increased the computational cost compared to equilibrium molecular dynamics simulations. Additionally, path integral methods have become a popular tool to account for the nuclear quantum effects present in systems that possess light molecules and low temperatures. We propose a method that will optimize the choice of parameters for umbrella sampling simulations that account for quantum effects via path integral methods. Specifically, we discuss the Path Integral Langevin Equation (PILE) thermostat [1] and the optimization of the centroid friction parameter as a function of the umbrella sampling biasing parameters. This methodology will be applied to the water dimer system using a version of the molecular modelling toolkit with the PILE thermostat [2] to study the impact of quantum effects on the free energy profile. We show that the large force constants required for the umbrella sampling impact the convergence of energy with respect to the path integral beads. We produce both the classical and quantum potentials of mean force for the water dimer system for a range of temperatures. The classical and quantum potential of mean force well depths are used to show the quantitative difference as a function of temperature. Finally, the second virial coefficients are calculated from the free energy profiles and compared to relevant literature values that use similar water models.

[1] M. Ceriotti, M. Parrinello, T. E. Markland, and D. E. Manolopoulos, *J. Chem. Phys*. **133**, 124104 (2010).
[2] C. Ing, K. Hinsen, J. Yang, T. Zeng, H. Li, and P.-N. Roy, *J. Chem. Phys.* **136**, 224309 (2012).

Simple relationships among molecular properties by analysis of the TABS database

Shamus A. Blair and Ajit J. Thakkar
Chemistry, University of New Brunswick

The TABS database [1] of minimum energy structures for 1641 molecules is constructed at the B3LYP/aug-cc-pVTZ level. The molecules all contain one or more C atoms and may have one or more H, N, O, F, S, Cl, and Br atoms. The molecules contain up to 34 atoms and 246 electrons. The database contains at least 25 molecules representing each of 24 functional categories. The database provides a reasonably large, moderately accurate, balanced, and consistent set of molecular structures that is useful for the study of relationships among properties of molecules of organic, biochemical, and pharmaceutical interest. Qualitative arguments and examination of numerical results for the TABS database are used to establish semiquantitative relationships between the size of a molecule and some of the moments of its electron momentum density [2]. The peak height of the Compton profile correlates well with molecular size and volume. Surprisingly, the molecular volume enclosed by the 0.001 a_0^{-3} isodensity contour of the electron number density can be predicted, with a mean absolute error of 2.1%, from $\langle 1/p^2 \rangle$. Semiquantitative relationships between the mean static dipole polarizability and other molecular properties such as the volume, ionization energy, electronegativity, and hardness are explored [3].

[1] S.A. Blair and A.J. Thakkar, *Comput. Theor. Chem*., in press (2014).
[2] S.A. Blair and A.J. Thakkar, *Chem. Phys. Lett*., submitted (2014).
[3] S.A. Blair and A.J. Thakkar, *J. Chem. Phys*., submitted (2014).

Orbital optimization techniques for the antisymmetric product of 1-reference-orbital geminals

Katharina K. Boguslawski, Pawel P. Tecmer and Paul W. Ayers
Department of Chemistry and Chemical Biology, McMaster University

The correlation energy is a central quantity in quantum chemistry. Although there exist no rigorous distinction between different types of electron correlation effects, the correlation energy is typically divided into two categories: strong (static and nondynamic) and weak (dynamic) [1].

While dynamic electron correlation effects can be accurately described by standard, well-established methods, like Möller-Plesset perturbation theory or single-reference coupled cluster theory, present-day quantum chemistry lacks simple, robust and efficient algorithms for a qualitatively correct description of strongly-correlated many-body problems.

Recently, we presented a conceptually different approach that is well-suited for strongly correlated electrons, but does not use the orbital model. Our method exploits the feature that electron correlation effects can be build into the many-electron wave function using two-electron functions, also called geminals [2]. One of the simplest practical geminal approaches is the antisymmetric product of 1-reference-orbital geminals (AP1roG) [3,4]. Yet, to ensure size-consistency, the one-particle basis functions need to be optimized.

In this work, we present a variational and different non-variational orbital-optimization protocols for AP1roG [4,5]. The non-variational orbital optimization schemes exploit the generalized Brillouin theorem for multiconfigurational self-consistent field wave functions as originally formulated by Levy and Berthier. The performance of the proposed orbital-optimization protocols is assessed against common multi-reference problems in quantum chemistry.

[1] P.-O. Löwdin, *Phys. Rev.* **97** (1955) 1509.
[2] P. R. Surjan, A. Szabados, P. Jeszenszki, and T. Zoboki, *J. Math. Chem.* **50,** 534 (2012).
[3] P. A. Limacher, P. W. Ayers, P. A. Johnson, S. De Baerdemacker, D. Van Neck, and P. Bultinck, *J. Chem. Theory Comput.* **9,** 1394 (2013).
[4] K. Boguslawski, P. Tecmer, P.W. Ayers, P. Bultinck, S. De Baerdemacker, and D. Van Neck, *Phys. Rev.* **89,** 201106(R) (2014).
[5] K. Boguslawski, P. Tecmer Peter A. Limacher, Paul A. Johnson, P.W. Ayers, P. Bultinck, S. De Baerdemacker, and D. Van Neck, *J. Chem. Phys.* (2014) accepted; K. Boguslawski, P. Tecmer, P. A. Limacher, P. A. Johnson, P.W. Ayers, P. Bultinck, S. De Baerdemacker, and D. Van Neck, to be submitted.

The application of phase-space localized basis functions to the calculation of rovibrational energies in polyspherical coordinates

James Brown and Tucker Carrington
Department of Chemistry, Queen's University

Recently [1], it was shown that accurate energy levels can be computed using a pruned von Neumann (vN) basis whose functions are re-expanded in a sinc discrete variable representation (DVR) basis. This accuracy is not possible with the vN basis alone. Expanding the vN basis functions in a sinc DVR basis solved the long-standing convergence problem of phase-space localized vN functions. Equivalent accuracy was retained even after a substantial number of the basis functions were pruned, which is not the case when using the sinc DVR alone. We show that expanding the vN functions with any DVR produces a basis with similar properties, namely convergence and prunability. Previously, the vN basis has almost exclusively been applied to the Watson Hamiltonian due to difficulties with, boundary conditions, and evaluating kinetic energy matrix elements in polyspherical coordinates. We show that the ability to use any DVR with the vN basis removes these barriers and permits the calculation of rovibrational energies in polyspherical coordinates. We also show this new basis is conducive to obtaining rovibrational energies iteratively, and therefore larger systems.

[1] A. Shimshovitz and D. J. Tannor, *Phys. Rev. Lett*. **109**, 070402 (2012).

Effective bond strength indicators

Yuzhe (Stan) Chen[1], Guixiang Wang[2] and Yan Alexander Wang[2]
[1]Department of Chemistry, University of British Columbia;
[2]Department of Chemistry, Nanjing University of Science and Technology

To save time and computational resources, we have made an attempt to design reasonable yet simple structural indicators to identify weak chemical bonds, instead of performing numerous, tedious calculations of individual bond dissociation energies (BDEs) for all bonds within a molecule. Based on the commonly available structure-property indicators for bond strength, such as bond length, the Mulliken interatomic electron number, the Wiberg bond order, we have created several new bond-strength indicators that can be directly used to efficiently identify almost all weak bonds with BDE below 350 kJ/mol. Furthermore, our new bond-strength indicators are more sensitive, easier to calculate, and more universally applicable than those bond-strength indicators derived from the Bader Analysis, including electron densities at the bond critical points, bond path length, and integral of electron density over interatomic surface between atoms pairs.

Full empirical potential curves and improved dissociation energies for the $X^1\Sigma^+$ and $A^1\Pi$ states of CH^+

Young-Sang Cho and Robert J. Le Roy
Department of Chemistry University of Waterloo

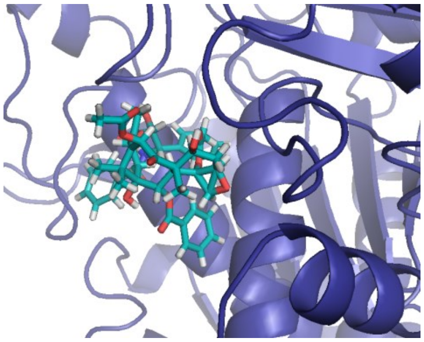
CH^+ has been a species of interest since the dawn of molecular astrophysics [1], and it is an important intermediate in combustion processes. In the domain of “conventional” spectroscopy there have been a number of studies of low v' and v'' components of the $A^1\Pi$–$X^1\Sigma^+$ band system of various isotopologues, plus a very recent heroic microwave study of the ground-state R(0) lines of $^{12}CH^+$, $^{13}CH^+$ and $^{12}CD^+$ [2]. In addition, Helm et al. [3] used photodissociation spectroscopy to observe transitions to very high-J’ tunneling-predissociation levels (shape resonances) involving v(A) = 0–10, for many of which they also measured the photo-fragment kinetic energy release. More recently Hechtfischer et al. used photodissociation spectroscopy of “Feschbach resonance” levels at very high v''(A) and low J to obtain the first direct estimate of the $^{12}CH^+$ dissociation energy with near-spectroscopic accuracy (±1.1 cm^{-1}) [4]. However, to date, all analyses of the data for this system had been performed using traditional band-constant fits, or Dunham-expansion treatments of the data for the lowest vibrational levels [5], and there have been no attempts to combine the “conventional” low-v data with the high-J'' and high-v'' photodissociation data in a single treatment. The present work has addressed this problem by performing a Direct-Potential-Fit (DPF) analysis that obtains full analytic potential energy functions for the $X^1\Sigma^+$ and $A^1\Pi$ states of CH^+ that are able to account for all of the available data (on average) within their uncertainties. Following comparisons with ab-initio results [6,7], a final X-state potential was obtained by including two mid-range ab-initio potential function values as pseudo “data” in the analysis.

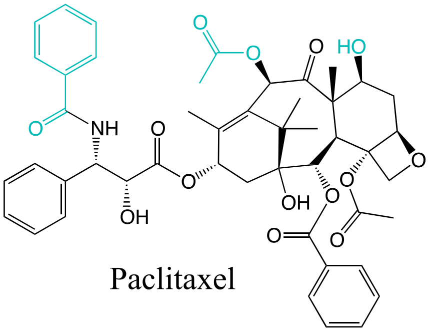
[1] A.E. Douglas and G. Herzberg, *Astrophys. J.* **94**, 381 (1941).
[2] T. Amano, *Astrophys. J. Lett.* **716**, L1 (2010).
[3] H. Helm, P.C. Crosby, M.M. Graff and J.T. Mosley, *Phys. Rev. A* **25**, 304 (1982).
[4] U. Hechtfischer, C. J. Williams, M. Lange, J. Linkemann, D. Schwalm, R. Wester, A. Wolf and D. Zajfman, *J.Chem.Phys.* **117**, 8754 (2002).
[5] H.S.P. Müller, *Astron. Astrophys.* **514**, L7 (2010).
[6] R. P. Saxon, K. Kirby and B. Liu, *J.Chem.Phys.* **73**, 1873 (1980).
[7] S. P. A. Sauer and V. Špirko, *J.Chem.Phys*. **138**, 024315 (2013).

Applying classical and quantum mechanics to study drug-protein interactions

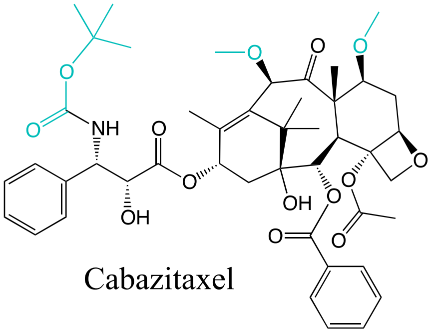
Cassandra D.M. Churchill[1], **Mariusz Klobukowski**[1] **and Jack A. Tuszynski**[2]
[1]Department of Chemistry, University of Alberta;
[2]Department of Oncology & Department of Physics, University of Alberta

The tubulin protein, which forms the microtubules that separate chromosomes during cell division, is a target for many cancer chemotherapeutics. The clinically-approved drugs Paclitaxel and Cabazitaxel share similar molecular frameworks with several functional group modifications. Classical dynamics simulations are used to explore differences in binding between these two drugs. Preliminary results, obtained using a fully quantum-mechanical model of tubulin-drug interactions via the Fragment Molecular Orbital method, are also presented and compared to the classical results.





Paclitaxel



Cabazitaxel

Materials mating game: Evolutionary optimization of nanoporous materials for CO_2 capture

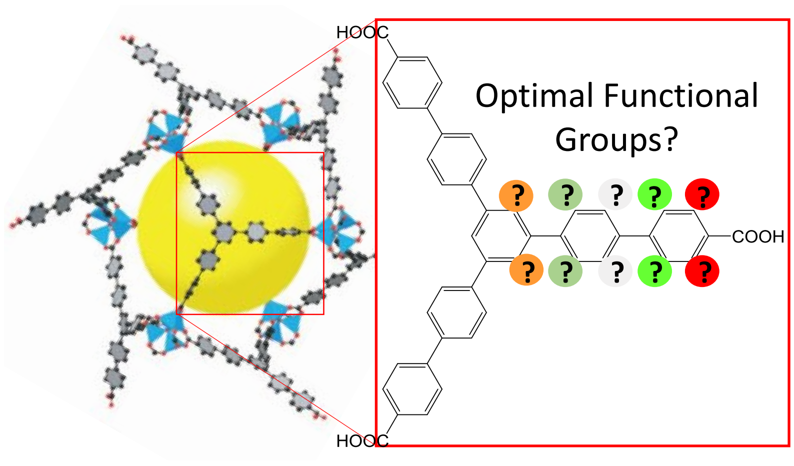
Sean P. Collins, Thomas D. Daff and Tom K. Woo
Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa

36 billion metric tons of CO_2 was released from the burning of fossil fuels in 2013 [1]. The capture and sequestration of CO_2 is a global challenge as world energy demands are expected to increase with fossil fuels being used as a major source. Metal-Organic Frameworks (MOFs) are a class of nano-porous materials that have been actively researched as a low cost solution for gas separation [2]. MOFs contain large internal surfaces and can be selective in adsorbing gases allowing a large amount of pure gas to be captured.

Adsorption properties of MOFs are tunable through functional groups although no correlation is known between functional groups and how they affect a MOF's adsorption properties [3]. Grand Canonical Monte Carlo simulations allow for accurate evaluations of adsorption properties in the matter of tens of minutes. The number of analogues of a MOF can often be over a million, making a full systematic evaluation of the space intractable.

In order to efficiently identify high performers, we developed a genetic algorithm (GA) to search the large functional group space. Using customized gene representations, mating and mutation algorithms we have been able to find the optimal functional group configuration by only sampling a fraction of all combinations. Using this approach we optimized the selectivity, adsorption and a combined figure of merit that measures the energy cost for CO_2 capture. For several well characterized MOFs, functional group configurations are predicted to give near record adsorption capacities at post-combustion CO_2 capture conditions.

[1] Le Quéré C. et al., *Global Carbon Budget 2013* (2013).
[2] Banerjee, R. et al. *Science* **319**, 939 (2008).
[3] Deng, H.; et al. *Science* **327**, 846 (2010).



The crystalloid structure of cellulose and its implications

Kevin M. Conley, Theo G.M. van de Ven and Tony Whitehead
Department of Chemistry, McGill University

Cellulose exhibits properties of chirality at various levels within the crystalline and fibril structure, but is not taken into account in the current model of crystalline cellulose. It is unknown how these properties arise on the molecular level. Molecular Orbital Theory predicts the minimum energy conformation of isolated cellulose chains deviate from the two-fold symmetry assumed in diffraction measurements. These small deviations result in a structure with multiple twist periodicities, including a right-handed twist of 4.1 nm and a left-handed twist of 75 nm. Semi-empirical, Hartree-Fock, and Molecular Dynamics calculations were performed on isolated cellulose molecules as well as small crystals with and without enforcement of two-fold symmetry.

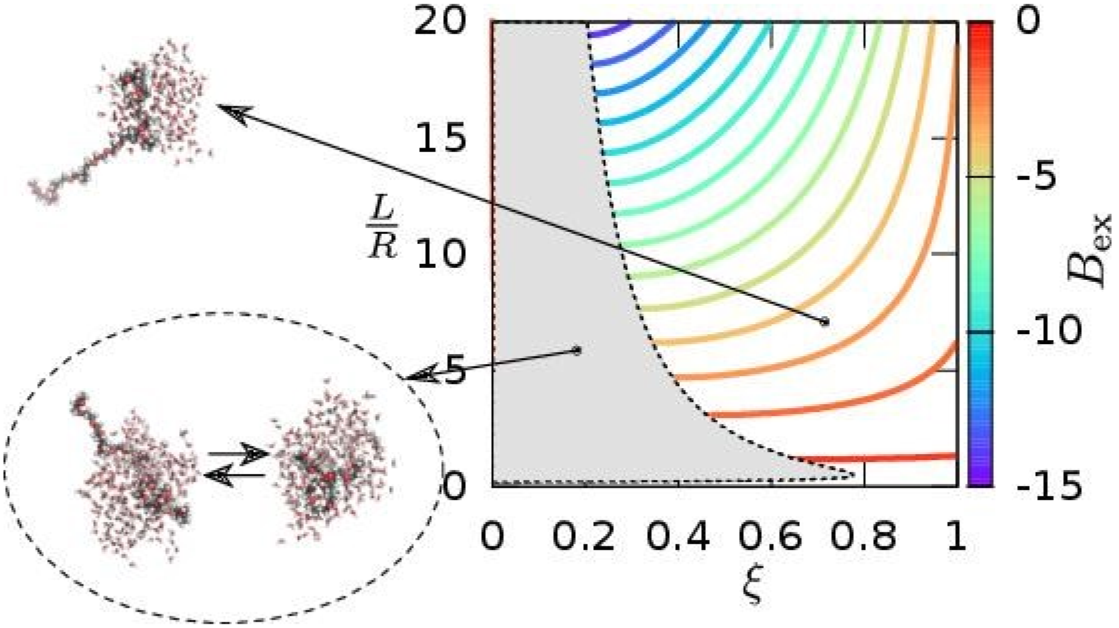
These twists lend support to a hypothesis formulated more than twenty years ago, namely that the cellulose nanocrystal is actually a distorted, right-handed “crystalloid”. Such a structure would explain, through Straley’s well-known model of close-packed screws, why liquid crystalline suspensions of cellulose are chiral nematic rather than the expected nematic. A twist could also explain the presence of periodic amorphous regions along cellulose nanofibrils. Long range twists have been observed microscopically in rare algal, animal and bacterial celluloses of large cross-sectional area, but cannot be observed directly on the smaller and more common cotton or wood celluloses. As modelling predicts that the twist increases with decreasing crystal cross-section, we present induced circular dichroism experiments to detect the amount of twist in cellulose crystals of varying sources, ranging from 20 X 20 nm to 3 X 3 nm.

Another important result of our modelling is that for very small arrays of cellulose chains initially arranged in the cellulose I-beta conformation, the distortions are such that we can no longer speak of a crystal or even a crystalloid. This may give insight into why cellulose crystals have a minimum cross-sectional dimension.

Macromolecule-ion interactions in droplets

Styliani Consta
Department of Chemistry, The University of Western Ontario

Recent theoretical and computational advances in the understanding of ejection mechanisms of solvated ions and charged macromolecules from highly charged nanodroplets are highlighted. While the physical basis for the instability leading to droplet fragmentation is relatively well understood, a description of the molecular mechanism of the fragmentation in complex systems is still missing. Development of a comprehensive model for the droplet fragmentation is further complicated by chemical modifications of the charged macromolecules (macroions) in changing droplet environment. Ejection of simple ions is analyzed using theory of activated processes. The presence of macromolecules adds a level of complexity into the system where the charge-induced instabilities cannot be described by a conventional theory such as Rayleigh or ion-evaporation mechanism. Additional charge-charge interactions between charged sites on a macromolecule dramatically change the macroion ejection mechanism. Molecular dynamics simulations reveal a number of distinct scenarios: contiguous extrusion, drying-out, star-like formation of solvent surrounding a macroion and pearl formation along the macromolecular chain. Each of the instabilities requires its own theoretical modelling to generalize the simulation findings.



Multicomponent dynamics of coupled quantum subspaces and field-induced molecular ionizations

Etienne Couture-Bienvenue and Jeremy Viau-Trudel
Département de chimie, Université Laval

To describe successive ionization steps of a many-electron atom or molecule driven by an ultrashort, intense laser pulse, we introduce a hierarchy of successive two-subspace Feschbach partitions of the N-electron Hilbert space, and solve the partitioned time-dependent Schrödinger equation by a short-time unitary algorithm. The partitioning scheme allows one to use different level of theory to treat the many-electron dynamics in different subspaces. A general program have been developed to treat laser-induced single ionization of many-electron molecules, implementing an L^2-functions-based Time-Dependent Configuration Interaction (TDCI) approach for bound-electrons in a neutral parent molecule and its cation, and a Volkov propagation of the freed electrons in the ionization continuum. Results of calculations on the six-electron BeH_2 molecule in a few cycle intense laser pulse will be shown to illustrate the functioning of the method. Computed photoelectron spectra are analyzed in terms of the energetics of the state-resolved ionization processes and in terms of molecular orbital (MO) structure of the molecule.

Kohn-Sham effective potentials from second-order reduced-density matrices

Rogelio Cuevas-Saavedra and Viktor N. Staroverov
Department of Chemistry, University of Western Ontario

A common approach to constructing the Kohn-Sham effective potential for a many-electron system is to use only the electron density. This methodology leads to some undesirable side effects such as unphysical oscillations and non-injective density-to-potential mapping in finite basis sets. Motivated by a recently developed algorithm for approximating the exchange-only optimized effective potential, we present an approach in which the second-order reduced-density matrix of the system is used to determine the corresponding exchange-correlation potential. The proposed algorithm is expected to be robust when tackling the density-to-potential mapping problem.

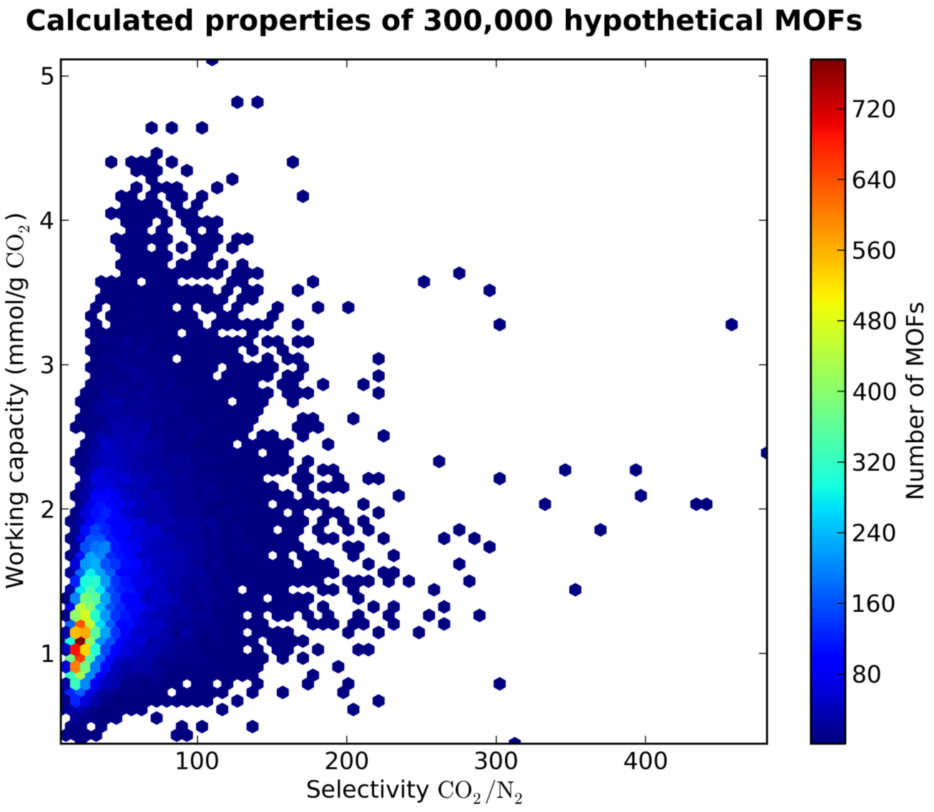
Screening the properties of millions of materials: High throughput virtual screening and materials informatics of MOFs

Thomas D. Daff, Peter G. Boyd, Michael Fernandez, Mohammad Zein Aghaji,
Sean P. Collins, Eugene S. Kadansev and Tom K. Woo
Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa

Power generation from fossil fuels accounts for 40% of global CO_2 emissions, having a major impact on global climate change. Carbon capture and storage (CCS) from the flue gas represents a practical strategy to reduce emissions in the near term, but scrubbing CO_2 is energy intensive, and hence expensive, due to regeneration of the sorbent material. Metal-organic frameworks (MOFs) have attracted significant attention as solid sorbents since they can possess extremely large uptake capacities with lower regeneration costs. MOFs present an almost infinite design space with innumerable combinations of inorganic, organic and functional group secondary building units (SBUs) being able to combine to form a MOF structure. With no simple link between the design and their performance as a gas capture material, experimental design becomes prohibitively labour intensive. Instead we can virtually screen vast numbers of new, hypothetical materials, computationally, for high performance.

We have developed a number of novel computational tools that allow us to design and optimise prospective MOFs, with high accuracy. We have algorithms to build new MOFs from component SBUs to expand known topologies or explore new ones. When combined with an algorithm to switch out functional groups from a large library, we can generate an almost limitless number of hypothetical initial structures, but with a focus on providing plausible synthetic targets. We have optimised our brute force screening (for example, parameterising the atomic partial charge calculation to give near ab-inito results in a fraction of the time) and we are able to calculate properties for hundreds of thousands of MOFs a day. We have also gone beyond brute force methods by implementing a fine-tuned evolutionary algorithm that will optimise the positions and combinations of functional groups within individual MOFs to optimise any property, or combination of properties that we can calculate. This algorithm can increase the efficiency that we find high performing materials by a factor of 50 or more and has found over a thousand high performing materials derived from synthetically known structures. Furthermore, we have used machine learning to analyse our results and have developed models that can tell us, with high success, whether a MOF will be a high performer without doing any calculations, opening the possibility to screen orders of magnitude more materials. Finally, for the highest performing materials, we are doing in-depth analysis of guest molecule binding sites and the structural features that give rise to binding sites so that we can adapt our methods to suggest more high performing CCS materials.

Continued…


Calculated properties of 300,000 hypothetical MOFs
Working capacity (mmol/g CO_2)
5
4
3
2
1
Selectivity CO_2/N_2
100
200
300
400
Number of MOFs
720
640
560
480
400
320
240
160
80

Density-functional description of electrides

Stephen G. Dale[1], **Alberto Otero-de-la-Roza**[2] **and Erin R. Johnson**[1]
[1]Department of Chemistry and Chemical Biology, University of California, Merced;
[2]National Institute for Nanotechnology, National Research Council of Canada

Electrides are a relatively-unexplored class of materials derived from research into solvated electrons. An electride is an ionic substance in which a confined electron, localised within a crystal void, acts as the anion. The localised electron gives electrides a number of unique properties including; high hyperpolarisabilities, high magnetic susceptibilities, highly variable conductivities, extremely low work functions, low-temperature thermionic emissions and very strong reducing character.

This study uses density-functional theory to investigate a range of electrides. Specifically, the band structure of these electrides is calculated allowing for identification of a high lying "electride" state, showing it is a consistent feature for electrides. A range of visualisation techniques are applied, including; plots of valence densities, procrystal densities, non-covalent interactions and Bader's quantum-chemical topology. All of these methods provide consistent results, confirming the localisation of electrons in each electride and demonstrating common electronic structure features throughout.

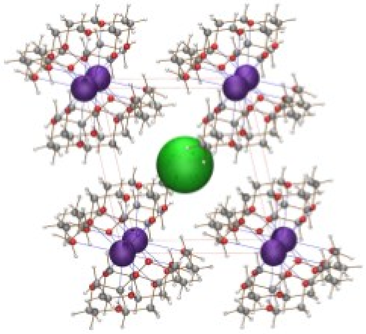


Figure 1: The crystal structure of $Cs^{+}(15\text{-crown-}5)_2e^{-}$, the simplest organic electride, with a representative sphere placed at the approximate electron location.

Conformation and energy analysis of sugars using path integral molecular dynamics

Nabil F. Faruk
Department of Chemistry, University of Waterloo

Quantum nuclear effects may be important in determining structural and thermodynamic properties for certain systems. To account for these effects, our group has previously incorporated path integral representation of nuclei into the Molecular Modelling Toolkit (MMTK) to enable Path Integral Molecular Dynamics (PIMD) simulations [1]. The purpose of this work is to provide a proof-of-concept for our software tools and PIMD method through the gas phase investigation of methyl beta-D-arabinofuranoside, which is a sugar residue in the cell wall of tuberculosis bacteria and is thought to provide bacterial resistance to drugs. We observe the effect of nuclear quantum sampling on the sugar's dihedral angle distributions at different temperatures, which we then relate to NMR proton-proton coupling constants via Karplus equations. We also determine the sugar's energy convergence with path integral sampling and the energy behaviour with temperature. We find that quantum effects are non-negligible even at biological temperatures. Finally, we discuss and benchmark our extension with the Open Molecular Mechanics (OpenMM) program to enable GPU-accelerated solution phase simulations for future work.

[1] C. Ing, K. Hinsen, J. Yang, T. Zeng, H. Li and P.-N. Roy, *J. Chem. Phys*. **136**, 224309 (2012).

DFT study of indium carbide clusters

René Fournier
Department of Chemistry, York University

A recent experimental study of indium carbide clusters [1] showed formation of various $In_mC_n^+$ species (m=1-21, n=1-9) when a indium surface is bombarded with keV $C60^-$ ions. Electronic structure calculations were performed on $In_mC_n^+$ (m=3,4, n=1-8) [1]. We extended those calculations by doing global geometry optimization with DFT (B3P86 exchange-correlation with a SDD basis set) for those same species, and also for $In_mC_n^+$ m=5-13 and n=0-3. The geometric structures of neutral and positively charged indium clusters are significantly different from those of aluminum clusters of the same size. The calculated cohesive energies of indium clusters follow a simple trend and extrapolate to a bulk value of 2.30 eV/atom, close to the experimental value of 2.52 eV/atom. The $In_mC_n^+$ clusters consist of a C atom, dimer or linear trimer "solvated" by In atoms. We find a large free energy change for the reaction 2 $In_3C_2^+$ --> In_3C^+ + $In_3C_3^+$, in line with the large abundance of $In_3C_2^+$. The $In_mC_2^+$ species are predicted to be thermodynamically stable with respect to various fragmentation channels: the absence of $In_mC_2^+$ (m>8) peaks in the mass spectra remains puzzling.

[1] J. Bernstein *et al.*, *J. Phys. Chem. A* **117,** 11856 (2013).

The role of hydrogen bonding in the decomposition of H_2CO_3 in water: Mechanistic insights from ab initio metadynamics studies of aqueous clusters

Mirza Galib
Department of Chemistry, University of Alberta

Both concerted and step-wise mechanisms have been proposed for the decomposition of H_2CO_3 in bulk water based on electronic structure and *ab initio* molecular dynamics calculations. To consistently determine which, if any, mechanism predominates in bulk water, we performed *ab initio* metadynamics simulations of the decomposition of H_2CO_3 in water clusters of increasing size. We found that in the small clusters (containing 6 and 9 water molecules), the decomposition occurs according to a concerted proton shuttle mechanism via a cyclic transition state, whereas in the larger clusters (containing 20 and 45 water molecules), the decomposition occurs according to a two-step mechanism via a solvent-separated HCO_3^-/H_3O^+ ion pair intermediate. Due to the additional water molecules in the larger clusters, the dissociation of H_2CO_3 into the metastable solvent-separated ion pair was found to be energetically favourable, thereby preventing the formation of the cyclic transition state and committing the decomposition to the sequential route. An analysis of the solvation environment around the H_2CO_3 molecule in the various clusters revealed that the transition from the concerted mechanism to the step-wise mechanism precisely hinges upon the number of water molecules hydrogen bonded to the H_3O^+ intermediate, which changes as the size of the cluster increases. The larger clusters contain a sufficient number of water molecules to fully solvate the H_3O^+ intermediate, indicating that they can provide a bulk-like environment for this reaction. Therefore, these results strongly demonstrate that the decomposition of H_2CO_3 in bulk water occurs via the step-wise mechanism.

Latest development in LIST methods

Miguel Angel Garcia Chavez and Yan Alexander Wang
Department of Chemistry, University of British Columbia

Following the success of the LISTi [1] and LISTb [2] methods to accelerate SCF calculations developed by our group, we introduce here two new faster methods, LISTf and fDIIS, which decrease the number of iterations needed to reach SCF convergence for some systems. While the performance of all LIST methods sensitively depend on the length of the LIST expansion vector, we found a way to overcome such an obstacle so that all latest LIST methods can consistently produce satisfactory results. Overall, the performance of our LIST methods either matches or surpasses the EDIIS+DIIS method [3] for all the systems in our investigation.

[1] Y. A. Wang; C. Y. Yam; Y. K. Chen and G. H. Chen, *J. Chem. Phys*. **134,** 241103 (2011).
[2] Y. K. Chen and Y. A. Wang, *J. Chem. Theory Comput*. **7,** 3045-3048 (2011).
[3] A. J. Garza and G. E. Scuseria*, J. Chem. Phys*. **137,** 054110 (2012).

The Photophysical Properties of Modified Emissive RNA Nucleobases: A Computational Study

Melis Gedik and Alex Brown
Department of Chemistry, University of Alberta

The use of fluorescent nucleic acid base analogues has become increasingly prevalent in the field of biotechnology, in particular for single-molecule detection of nucleic acids. The advantages of utilizing isomorphic emissive nucleobases for biophysical assays is that they can be incorporated into nucleic acids with minimal perturbation to the native structure, are well localized, and sensitive to the microenvironment. One such class of analogues have been designed and developed by Tor et al [1] which employ the [3,4-d]-pyrimidine heterocyclic nucleus and represent a complete alphabet of emissive nucleobases. In this work, extensive computational study of the photophysical properties of modified nucleobases will be presented. This work includes an analysis of the charge transfer character, absorption and emission profiles of the modified analogues, which are then compared to their naturally occurring non-emissive counterparts [2]. The theoretical results from this particular study demonstrate excellent agreement with experimental data [1]. In addition, interaction energies, Watson-Crick bonding parameters as well as optical absorption for the base pairing between natural-modified and modified-modified nucleobases is reported. Finally, a comparison of the various computational methods used for determination of the aforementioned properties will be offered.

Optimizing fractional orbital occupations in Kohn-Sham DFT

Cristina E. González Espinoza and Paul W. Ayers
Department of Chemistry and Chemical Biology, McMaster University

Systems with strong (static) correlation represent a great challenge to Kohn-Sham density functional approximations (KS-DFA)[1]. Bond-breaking reactions, transition metal compounds and conjugated polymers are examples of strong correlated systems, characterized by a small gap between the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO). Is in these cases where fractional orbital occupations arise[2].

In this work we propose a method to optimize the orbital occupation numbers. We use a limited memory Broyden–Fletcher–Goldfarb–Shanno[3] method with box constraints (L-BFGS-B) to force the occupation numbers to have values between 0 and 1, and optimize an augmented Lagrangian for the normalization condition.

[1] A. J. Cohen, P. Mori-Sánchez, and W. Yang, *Chem. Rev.*, **112**, 289-320 (2012).
[2] A. J. Cohen, P. Mori- Sánchez , and W. Yang, *J. Chem. Phys.*, **129**, 121104 (2008).
[3] C. Zhu, R. H. Byrd and J. Nocedal, *ACM Transactions on Mathematical Software*, **23 (4)**, 550-560 (1997).

The study of the fragmentation of molecular ions in intense and short laser field

Salima S.H. Hennani[1] and Samira S.B. Barmaki[2]
[1]Département de Chimie, Université Laval;
[2]Département de physique, Université de Moncton

A theoretical treatment is presented of the dynamics of a homo- and/or hetero-nuclear one-electron diatomic molecule exposed to an intense laser pulse. In a basis of B-spline functions of appropriate elliptical variables, we first calculate the electronic structure of the field-free molecule, including bound states as well as an extensive series of states in the ionization continuum. We then solve numerically the time-dependent Schrödinger equation (TDSE) for the laser-driven molecule by a spectral approach, i.e. in the basis of the field-free energy eigenstates. Above Threshold Ionization (ATI) spectra of the laser-driven H_2^+ molecule are calculated at different laser intensity and frequency conditions. We study in particular the ionization and electronic excitation of the H_2^+ ion as a function of frequency chirp parameters. We illustrate how population transfer from the molecular ground state to different excited states depends on these frequency chirp conditions, and in turn governs the ionization dynamics.

The validity of the decomposition of the dispersion energy into atom-atom contributions

Joshua W. Hollett[1] **and Peter M.W. Gill**[2]
[1]Department of Chemistry, University of Winnipeg;
[2]Research School of Chemistry, Australian National University

The MP2 energy of 1-D and 2-D infinite lattices, and an infinite 1-D array of infinitely long strings, of simplified He atoms is calculated in a Wannerized basis at varying atomic separations. The MP2 energy is decomposed into dispersion, atom-atom dispersion and more-than-two-atom dispersion components. The more-than-two-atom component is essentially zero beyond 1.5 times the equilibrium separation of the atoms in the 1-D and 2-D lattices. The increased rate of growth of the more-than-two-atom component, as atomic separation decreases, with increased dimensionality is due to a Jacobian effect. For infinitely long strings at large separations (1-D and 2-D arrays), the more-than-two-atom component of the total MP2 dispersion energy is 9%.

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

Radu Iftimie
Department of Chemistry, University of Montreal

We investigate the proton transfer mechanisms involved inside aqueous, solvent-separated encounter complexes between phenol and carboxyl moieties using Ab-Initio molecular dynamics (AIMD) and computational time-resolved vibrational spectroscopy. This model frame-work can be viewed as a ground-state analog of the excited state proton transfer reactions that have been actively investigated using ultrafast spectroscopy. The results presented represent a significant step forward in the molecular level understanding of the diverse processes involved in proton transfer within water separated encounter complexes. The AIMD complements the experiments extremely well, giving access to details of the underlying mechanisms that are difficult (or impossible) to obtain from the experimental data alone. As a result, we are able to unify seemingly disparate experimental observations.

In particular, three qualitatively distinct proton transfer pathways are observed in the simulations which can be described as direct concerted, direct sequential and through bulk transfers. The primary difference between the sequential and concerted mechanism is the involvement of a reaction intermediate in which the proton fluctuates for several picoseconds through the hydrogen bonds connecting donor and acceptor, but resides primarily on an intervening water molecule in the encounter complex. An important feature of this work is that it shows there are a diversity of qualitatively different underlying PT mechanisms at work AND that basically all of these mechanisms have been discussed in the associated experimental literature.

Particle entanglement in quantum clusters: Rényi entropy via the permutation operator

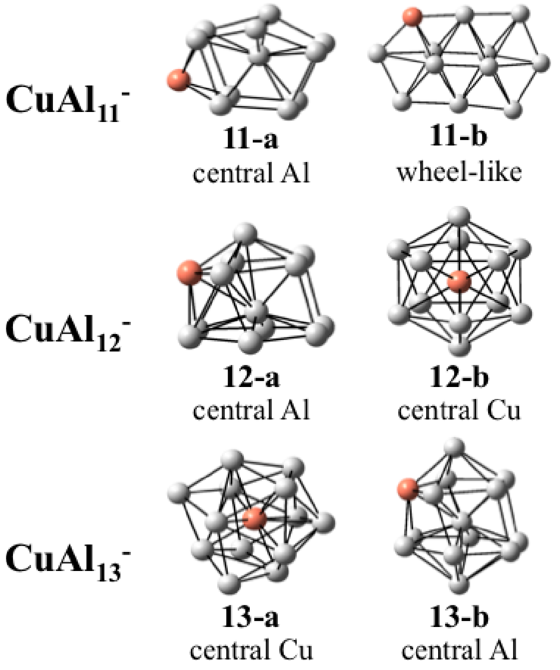
Dmitri Iouchtchenko, Matthew Schmidt and Pierre-Nicholas Roy
Department of Chemistry, University of Waterloo

Quantum clusters have been observed to exhibit superfluid-like behaviour, which could have an impact on the discovery of a new superfluid and on elucidating the mechanisms behind superfluids in general. In order to better understand this phenomenon, we wish to use Path Integral Molecular Dynamics (PIMD) to study the entanglement entropy of quantum clusters. Specifically, we will use the zero temperature variant of PIMD known as Langevin equation Path Integral Ground State (LePIGS), which is implemented in the Molecular Modelling Toolkit (MMTK) software. The suggested technique will make use of two replicas of the system and will permute bead coordinates between these replicas in order to estimate the Rényi entropy. Current research is focused on developing the method and benchmarking it using a system of two coupled harmonic oscillators for which analytic expressions can be derived. Once the method is shown to be reliable, it will be applied to quantum clusters (e.g. para-hydrogen clusters) to obtain information about entanglement of physical systems.

Theoretical study on the relationship between geometric feature and electronic behavior of aluminum cluster doped copper atom

Chiaki Ishibashi, Kaoru Onoe and Hidenori Matsuzawa
Department of Life and Environmental Sciences, Chiba Institute of Technology

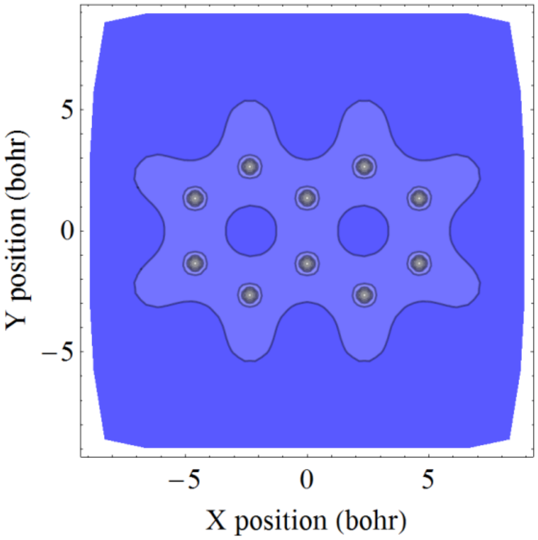
There are many reports of geometric and electronic structures for the Al cluster doped heteroatoms. The electronic feature of the cluster depends on the cluster size, geometry and doped atoms, generally. The electronic structure for the Al cluster doped Cu atom are reported in this presentation. After the geometry optimization of the $CuAl_n^-$ (n=11-13) clusters using B3LYP method with 6-311+G* basis set, the partial density of states (PDOS) of the clusters were obtained. In $CuAl_n^-$ (n=11-13) clusters, the geometric change occurs with the increasing of Al atom. The electronic structures depend on the framework structure and position of Cu atom in the clusters. The most stable structure and low-lying isomer of the $CuAl_n^-$ (n=11-13) clusters are shown in figure. The framework of n=11 and 12-13 is wheel-like and icosahedral, respectively. The Cu atom locates at center (12-b, 13-a) or on surface (12-a, 13-b), of the icosahedral framework. In the case of 12-b and 13-a, complete s-d hybridization of surrounding Al and central Cu atoms occurs. On the other hand, the incomplete hybridization is found in 11-a and 13-b. The shell structure of 11-b and 12-a is incomplete. On the basis of these results, we succeeded in the investigation of the relationship between the geometric feature and the electronic behavior of the $CuAl_n^-$ (n=11-13) clusters.



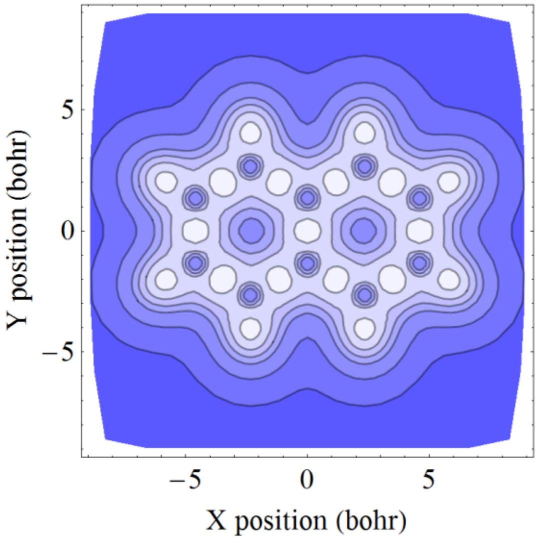
How far do electrons delocalize?

Benjamin G. Janesko[1], Giovanni Scalmani[2] and Michael J. Frisch[2]
[1]Department of Chemistry, Texas Christian University; [2]Gaussian Inc.

Electron delocalization is central to chemical bonding, but it is also a fundamentally nonclassical and nonintuitive quantum mechanical phenomenon. We develop a new approach to quantify and visualize delocalization in real space. Our electron delocalization range function EDR(r;u) quantifies the degree to which electrons at point r in a calculated wavefunction delocalize over length scale u. The plot below illustrates EDR(r,u) in the atomic plane of naphthalene. EDR(r, u=0.25 bohr) is large in the carbon atom cores, consistent with localization of core electrons to around 0.25 bohr. EDR(r, u=1 bohr) is large in C=C and C-H bonds, consistent with electron delocalization across the length of the bond. Applications are presented to atomic shell structure; covalent and ionic bonding; electron delocalization in excited states, defects, and solvated electrons; and post-Hartree-Fock models of strong correlation.



Naphthalene EDR(r,u=0.25 bohr)



Naphthalene EDR(r,u=1.00 bohr)

C-C bond activation upon protonation of the TEMPO$^\bullet$ nitroxyl radical

Soran Jahangiri[1], Qadir K. Timerghazin[2], Heng Jiang[1],
Ann M. English[1] and Gilles H. Peslherbe[1]
[1]Centre for Research in Molecular Modeling (CERMM)
and Department of Chemistry and Biochemistry, Concordia University;
[2]Department of Chemistry, Marquette University

The stable nitroxyl radical (2,2,6,6-Tetramethylpiperidin-1-yl)oxy, TEMPO$^\bullet$, and its derivatives are widely used as spin labels, catalysts in organic synthesis, polymer stabilizers and antioxidants. Electrospray ionization mass spectrometry of TEMPO$^\bullet$ under various conditions revealed facile loss of the CH3$^\bullet$ radical from the protonated TEMPOH$^{\bullet+}$ odd-electron ion while the even-electron TEMPO$^+$ and TEMPOH$_2^+$ ions fragment via the expected C–N bond cleavage, releasing NH_2OH. Experimental data thus suggest that protonation of TEMPO$^\bullet$ leads to dramatic C–C activation and formation of highly reactive $CH_3^\bullet$ radicals. Density-functional theory calculations and direct dynamics simulations were performed to provide insight into the relative stabilities of the TEMPO$^\bullet$ ions. The computational results confirm the activation and facile cleavage of the C–CH_3 bond of TEMPOH$^{\bullet+}$ upon collision while C–N bond dissociation is observed for the TEMPO$^+$ and TEMPOH$_2^+$ ions.

The dynamic behavior of CO under high temperature and pressure

Guangfu Ji[1], Dongqing Wei[2] and Xiaofeng Li[1]
[1]Lab for Shock wave and Detonations Physics, Institute of Fluid Physics;
[2]College of Life Sciences and Biotechnology, Shanghai Jiaotong University

Carbon monoxide (CO) is one of the simplest heteronuclear diatomic compounds and has a high abundance in nature. CO and N_2 are the isoelectronic system, which have the same size and weight, similar boiling point and liquid density, nearly the same Hugoniot curves below 10GPa. Being one of the explosive denotation products CO, is a very sensitive compound and becomes unstable at 5GPa and room temperature. While N_2, is stable up to 180GPa. Though the chemical reactions and properties of solid CO have been investigated under pressures. There are few reports about the properties of the gas CO under high pressure and temperature. Here we reported the complicated results of gas CO reactions under high pressure and temperature by MD method.

Geometric phase effects in high-dimensional nuclear quantum dynamics near conical intersections

Loïc Joubert-Doriol[1], Ilya G. Ryabinkin[2] and Artur F. Izmaylov[1]
[1]Department of Physical and Environmental Sciences, University of Toronto at Scarborough;
[2]Chemical Physics Theory Group, Departement of Chemistry, University of Toronto

Conical intersections (CIs) play an important role in photochemistry by facilitating non-radiative electronic transitions. Another prominent feature associated with CIs is the appearance of a nontrivial geometric phase (GP) in nuclear and electronic wave-functions in the adiabatic representation. It was found that including the GP in dynamical simulations of a two-dimensional linear vibronic coupling (LVC) model can drastically modify nuclear dynamics by reducing the population transfer between the minima of the lower energy adiabatic surface [1]. However, it was not clear whether this purely quantum effect would survive in the presence of dissipative environment. To address this question we study GP effects in high-dimensional LVC models using a subsystem-bath partitioning within a generalized master equation formalism. It is found that GP effects can survive in dissipative environment, and we devise simple rules to determine the significance of the GP for nuclear dynamics of a general LVC model.

[1] I. G. Ryabinkin and A. F. Izmaylov, *Phys. Rev. Lett*. **111**, 220406 (2013).

Mulliken population analysis of organic & inorganic systems using atomic orbital basis sets

Taewon D. Kim, Farnaz Heidar-Zadeh and Paul W. Ayers
Department of Chemistry and Chemical Biology, McMaster University

Mulliken population analysis, while simple and mathematically elegant, often gives chemically unreasonable charges and erratic trends for large basis sets, especially if the basis sets include diffuse functions. Mulliken population analysis gives reasonable results for small (e.g., minimal) basis sets. These basis sets, however, are often unable to accurately model the molecule's electronic structure. For single-determinant methods, Ruedenberg's quasiatomic minimal basis set orbitals (QUAMBO)[1] and Knizia's intrinsic atomic orbitals (IAO)[2] give minimal basis sets composed of orbitals that (i) resemble the isolated-atom orbitals and (ii) span the space of the occupied molecular orbitals. In this study, we re-expressed the molecular density matrix in one of these minimal atomic orbital basis sets, then performed Mulliken population analysis. This poster reports the basis-set sensitivity and chemical integrity of these generalized Mulliken charges for a diverse set of 168 drug-like organic molecules and 41 main-group inorganic molecules, for a variety of basis sets (STO-6G, SVPD, TZPD, QZPD) .

[1] W. C. Lu, C. Z. Wang, M. W. Schmidt, L. Bytautas, K. M. Ho and K. Ruedenberg, *J. Chem. Phys*. **120(6)**, 2629 (2004).
[2] Knizia, G. *J. Chem. Theory Comput*. **9**, 4834 (2013).

Average local ionization energy as a generalization of the electrostatic potential

Sviataslau V. Kohut and Viktor N. Staroverov
Department of Chemistry, University of Western Ontario

The average local ionization energy (ALIE) introduced by the Politzer group has found wide applications in computational chemistry. Although the ALIE was originally defined in terms of the Hartree-Fock or Kohn-Sham orbitals and corresponding eigenvalues, one can write it as a sum of the electrostatic potential, the local kinetic energy density per electron, and the exchange-correlation potential. Thus, the ALIE can be viewed as a generalization of the electrostatic potential for quantum systems. We analyze the role each of these terms plays in making the ALIE a useful descriptor of chemical reactivity.

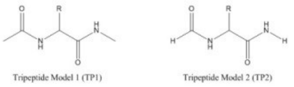
Study of the repair mechanism of aliphatic amino acids with dihydrolipoate using two tripeptide models

JinGyu Lee, Romina Castañeda, J. Raúl Alvarez-Idaboy and Nelaine Mora-Diez Diez
Department of Chemistry, Thompson Rivers University

Free-radicals are constantly produced in the human body and a variety of antioxidant species control their production under normal functioning conditions. When this balance is broken, excess radical species accumulate and can severely damage the organism. In terms of proteins and enzymes, the main target of free radicals can either be the protein backbone or the side chains on the amino acids. Lipoic acid, an organosulfur compound, is one of the antioxidants present in the human body, more abundant in its deprotonated form under physiological pH. The lipoate anion is related by a redox equilibrium with dihydrolipoate, its reduced form (DHL), which has two possible repair sites (the two thiol groups, -SH).

This computational study focuses on the repair mechanism of damaged aliphatic lateral chains of proteins with DHL. To simplify the modeling of the protein backbone, two tripeptide models (with an aliphatic amino acid in its lateral chain) were used, see Figure 1. The lateral chains studied are alanine, valine, and leucine with two, three, and four possible damaged sites, respectively. The repair reactions modelled involve the hydrogen transfer from DHL to the damaged site of the amino acid, initially in radical form. Calculations were performed at the M06-2X/6-31++G(d,p) level of theory. Transition states (TS) were calculated for the exergonic repair reactions (those for which $\Delta G^{o} < 0$); see Figure 2 for an example using the valine side chain. Rate constants were calculated applying classical transition state theory.

The results, using both tripeptides models, are compared and general trends for the $\Delta G^{\ddagger}$ and ΔG^{o} values are observed. The $\Delta G^{\ddagger}$ is smaller (and ΔG^{o} is more negative) the further away the repair site is from the carbonyl group. Thus, as the repair site is moved along the aliphatic chain, the rate constant of the repair reaction became larger.



Tripeptide Model 1 (TP1) Tripeptide Model 2 (TP2)

R = alanine, valine, leucine

Figure 1. Two tripeptide models observed with varying aliphatic lateral chains.

Figure 2. An example of a fully optimized transition state using the valine side chain.

The atomistic feature of molybdenum carbide nanocatalysts in the in-situ environment: A DFTB and QM(DFTB)/MM study

Xingchen Liu and Dennis R. Salahub
Department of Chemistry, University of Calgary

There is no doubt that a huge gap exists in understanding heterogeneous catalysis between a cluster model of a few atoms and a bulk model of periodic slabs; examples are nanocatalysts. On the other hand, the role of the solvent in modelling solid/liquid heterogeneous reactions is often neglected. In this work, we will present our recent results that attempt to fill the cluster-bulk gap by using the Density Functional Tight Binding (DFTB) method to study benzene hydrogenation reactions on different sizes of molybdenum carbide nanoparticles. The results show that a particular 2-fold site on a 1.9 nm nanoparticle is more active than 3-fold sites, and they are more active than 3-fold sites on 1.2 nm or 2.3 nm nanoparticles in benzene hydrogenation. The similar electronic structures reflected by the HOMO-LUMO gaps of the selected nanoparticles indicate that surface site is the dominant factor in the catalytic activity of these nanoparticles. The study was extended to consider a nanoparticle embedded in solvent (benzene), using a Quantum Mechanical (DFTB) / Molecular Mechanical approach. The inclusion of solvent was found to be very important in predicting the free energy profiles of such reactions.

A novel chemistry principle-based force field

Zhaomin Liu[1], Christopher R. Corbeil[2] and Paul Labute[2]
[1]Department of Chemistry, McGill University;
[2]Chemical Computing Group Inc.

In molecular mechanics, molecular potential energy is modeled by summing the bonding and non-bonding interactions computed through functions and a set of parameters, known as force fields. These parameters are traditionally derived from a large training set of small molecules/fragments and organized by atom types. However, their transferability to a variety of molecules such as potential drug candidates is poor due to this training-deriving philosophy. More specifically, electronic effects (i.e., hyperconjugation, conjugation) are very case dependent and can strongly affect their accuracy on the torsional energy profiles of rotatable bonds. Herein, we describe a conceptually new force field that understand and encode chemistry knowledge to derive specific parameters on-the-fly from atomic properties. Our method is not based on training and expected to be more transferable than generic atom type-based force fields.

Knots and their representations

Csongor Matyas, Raymond Poirier and Peter Warburton
Department of Chemistry, Memorial University of Newfoundland

An easy and efficient way is presented for describing knots in proteins. There are many polynomials for describing knots, but none of them are perfect, and they do not deal with different knot representations. This new method describes knots and all knot representations with matrices and polynomials and can distinguish between knots, chiral isomers, orientations, and identify the symmetry. Knots can be redrawn easily, knowing their matrices. This method can be used in examination of protein folding and similarity measures.

Relaxation and electron solvation dynamics of iodide-polar solvent molecule clusters

Chun C. Mak and Gilles H. Peslherbe
Centre for Research in Molecular Modeling (CERMM)
and Department of Chemistry and Biochemistry, Concordia University

Photoexcitation of iodide-polar solvent molecule clusters results in the transfer of an electron from an iodide localised orbital to a diffuse solvent cluster localised orbital, followed by extensive relaxation processes that are closely related to the electron solvation processes occurring in bulk polar liquids. Using femtosecond photoelectron spectroscopy, Neumark and co-workers have explored the relaxation dynamics of a variety of photoexcited iodide-polar solvent molecule clusters, $[I^{-}(Solv)_n]^*$, revealing a high degree of solvent specificity of the electron solvation dynamics.

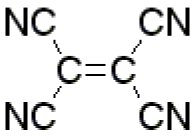
In the present work, high-level quantum chemical calculations and *ab initio* molecular dynamics simulations are used to elucidate the relaxation mechanism of $[I^{-}(Solv)_n]^*$ (Solv = H_2O, CH_3OH and CH_3CN) and gain molecular-level insights into the solvent specificity of the electron solvation dynamics. Results indicate that substantial solvent cluster reorganisation takes place in $[I^{-}(Solv)_n]^*$ during the relaxation process; clusters with a relatively stable network of solvent-solvent interactions, such as $[I^{-}(H_2O)_n]^*$, undergo rearrangement to stabilise and solvate the excited electron, while clusters lacking such features, such as $[I^{-}(CH_3OH)_n]^*$, tend to undergo fragmentation, ultimately resulting in destabilisation and ejection of the excited electron. Structural properties of the solvent molecules can thus exert a profound influence on the relaxation mechanism of $[I^{-}(Solv)_n]^*$, leading to the highly solvent specific nature of the cluster analogues of electron solvation processes.

Symmetry breaking in silicon analogues of TCNE and TCNQ

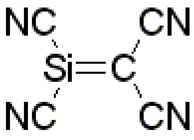
Steven M. Maley and Robert Mawhinney
Department of Chemistry, Lakehead University

Structural properties for a series of silicon analogues of tetracyanoethylene 1, 2, 3 (TCNE) and tetracyanoquniodimethane 4, 5, 6 (TCNQ) in various oxidation states (+1, 0, -1) were calculated using various density functionals and basis sets. Results calculated at the B3LYP/6-311++g(2df,pd) level of theory show the planar geometry is a minimum for uncharged 1, 2, 4 and 5 as well as all cations. Uncharged 3 [v_1=121i] and 6 [v_1=54i, v_2=44i] as well as the anions of 4 [v_1=270i] and 5 [v_1=226i] lead to geometries which are pyramidilized at the silicon atom(s). However, other functionals do not display the symmetry breaking effects. The observed symmetry breaking is explored from the pseudo Jahn-Teller perspective.

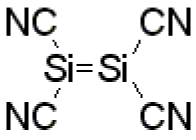
Tetracyanoethylene Series



(1)

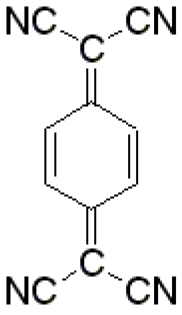


(2)

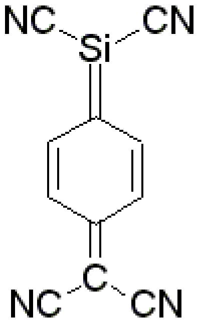


(3)

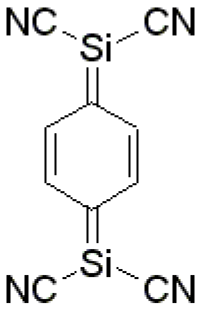
Tetracyanoquinodimethane Series



(4)



(5)



(6)

Assigning QCT results to quantum states: A closer look at binning methods

Margot E. Mandy and Seamus Hogan
Chemistry Program, University of Northern British Columbia

One of the ongoing issues in the quasiclassical trajectory method is the assignment of the outcome of the trajectory to a quantum state and the subsequent calculation of a cross section for a transition. A number of methods have been proposed with varying success, from the bin histogram method to the more recent Gaussian methods. It has been established that the bin histogram method gives rise to cross sections that are "hot" relative to experimental and full quantum results for atom-diatom systems [1]. This is aggravated when there are more quantum numbers involved. Recently there has been increased interest in Gaussian binning methods. Earlier attempts at Gaussian binning used separate distributions for each quantum number which gave rise to poor convergence, even with large batches of trajectories. More recent attempts utilize a single Gaussian distribution based on the energy of the quantum state, regardless of the number of quantum numbers involved [2]. A parameter related to the width of the Gaussian distribution must be determined. Is there a robust way arising from the physics of the system to select the value of the parameter? How many trajectories are necessary for satisfactory convergence? Can standard errors be determined? Does Gaussian binning offer an improvement over other methods? In addition to resolving the issue of "hot" cross sections, is detailed balance obeyed? Can it be translated robustly to systems with more quantum numbers?

This is explored and compared to other methods of determining cross sections for the He + H_2, H + H_2, and the H_2 + H_2 systems using an existing database of large batches of quasiclassical trajectories.

[1] M. E. Mandy, P. G. Martin, W. J. Keogh, *J. Chem. Phys.* **100**, 2671 (1994).
[2] R. Conte, B. Fu, E. Kamrchik, J. M. Bowman, *J. Chem. Phys.* **139**, 044104 (2013).

Assessing the performance of approximate solutions of the quantum-classical Liouville equation for simulating the dynamics of electron and proton transfer reactions

Franz Martinez and Gabriel Hanna
Department of Chemistry, University of Alberta

Mixed quantum-classical methods, which partition a system into a quantum subsystem and a classical environment, can be viable options for simulating the dynamics of systems for which a full quantum treatment is not feasible. Among these methods, the quantum-classical Liouville equation (QCLE) provides a rigorous approach but its solution in terms of an ensemble of surface-hopping trajectories has proven to be computationally demanding for simulating the long-time dynamics of both real and model systems. Two approximate solutions of the QCLE, namely the Poisson bracket mapping equation (PBME) solution and the forward-backward trajectory solution (FBTS), have proven to be computationally efficient but their accuracies depend on the nature of the system. We investigated the validity of these approximate solutions for simulating a simple model of a photo-induced electron transfer (ET) reaction and a more realistic model of a proton transfer (PT) reaction in a hydrogen-bonded complex in a polar nanocluster. When compared to the numerically exact results, we found that the PBME solution is not capable of qualitatively capturing the population dynamics of the ET model, whereas the FBTS is. Nevertheless, both methods are capable of qualitatively capturing the time-integrated transient absorption signal of this model. In the case of the PT reaction, PBME dynamics is not capable of capturing the well-defined covalent and ionic states of the complex, but rather exhibits an average of the two. Overall, our findings demonstrate that caution must be taken when applying these approximate methods, since they can manifest non-physical behaviour for systems which exhibit strong subsystem-bath couplings and/or where a mean-field-like description is not valid.

Theoretical study on reaction of metastable diacetylene with ground state propyne in Titan's atmosphere

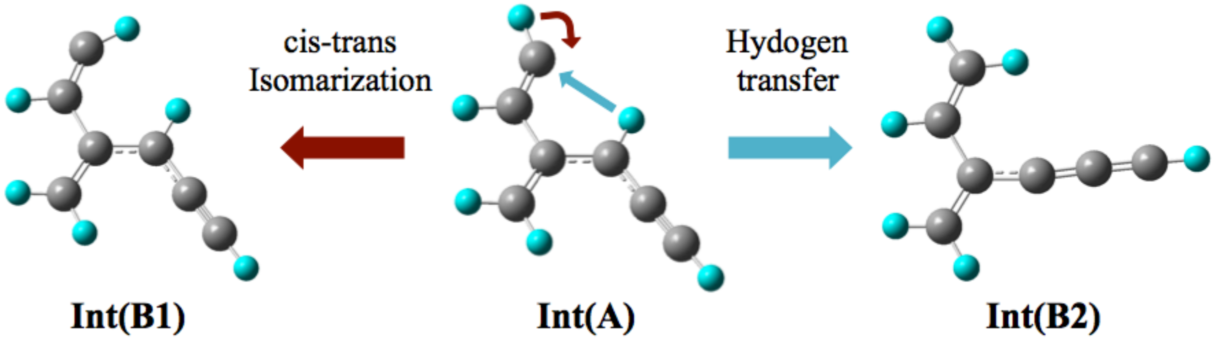
Hidenori Matsuzawa and Daisuke Nawata
Department of Life and Environmental Sciences, Chiba Institute of Technology

There is a haze layer including organic polymer and other organic compounds in Titan's atmosphere. Diacethylene plays an important role for the haze formation. The reaction of metastable diacethylene (C_4H_2*) with ground state propyne (C_3H_4) is noted as one of the key reactions for the haze formation. From the experimental study [1], it is confirmed that this reaction produces C_5H_4, C_5H_3 and other hydrocarbons.

$$C_4H_2^* + C_3H_4 \rightarrow C_5H_4 + C_2H_2 \text{ (and } C_5H_3 + C_2H_3\text{)} \quad (1)$$

We examined this reaction process theoretically. Calculation methods were B3LYP and CCSD with cc-pVDZ basis set. In this reaction, an intermediate (Int A) is formed through several reactions from reactants. The intermediate of C_5H_4 formation pathway (Int B1) is produced by the cis-trans isomerization of Int A. On the other hand, by the hydrogen transfer reaction of Int A, the intermediate of C_5H_3 formation pathway (Int B2) is formed. The Gibbs free energy (ΔG) of C_5H_4 or C_5H_3 formation is -27.2 or -27.0 kcal/mol, respectively, under the Titan's condition (180K, 0.001 atm).

[1] R. K. Frost et al., *J.Am. Chem. Soc.* **118**, 4451 (1996)

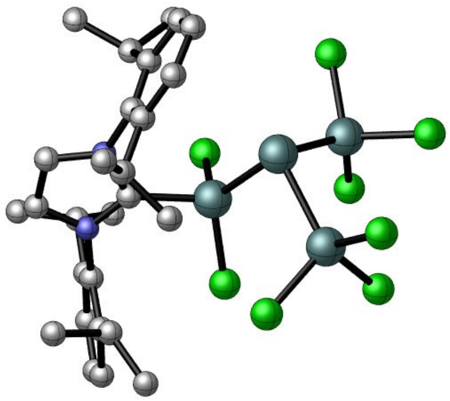


N-heterocyclic carbene/ylide supported $GeCl_2$ and GeH_2 complexes: Insights from theory

Mohammad Reza Momeni Taheri and Alex Brown
Department of Chemistry, University of Alberta

In searching for new oligomeric materials with desirable properties based on main group elements, Lewis base-supported germanium dichloride oligomers $(GeCl_2)_x$ (x = 2) were theoretically investigated [1]. Computational studies determined the relative energies of a series of carbene-capped linear and branched oligomers, IPr•$(GeCl_2)_x$ (x = 2-4) (IPr = $[(HCNDipp)_2C:]$; Dipp = 2,6-$iPr_2C_6H_3$). The branched structures were shown to be thermodynamically favoured upon increasing Ge content. Natural bond orbital (NBO) [2] analysis shows that the Wiberg Bond Index (WBI) for the Ge-Ge bonds in the linear Ge_4 array is on the order of 0.69, while much higher indices (0.90 to 0.92) are found in the branched array; thus branching appears to be partially driven by the formation of stronger Ge-Ge linkages. To explore the chemistry of heavier main group elements further, stable complexes of the elusive H_2GeGeH_2 in the form of a donor-acceptor coordination with suitable Lewis base/acid combinations (LB•H_2Ge-GeH_2•LA; LB = N-heterocyclic carbene or N-heterocyclic olefin; LA=$W(CO)_5$) were investigated [3]. The nature of the bonding in these species was examined by NBO and atoms in molecules (AIM) [4] analyses. These data point toward the presence of polar covalent Ge-Ge single bonds in the hindered digermene complexes and dative Ge-C interactions between the digermene and the carbon-based Lewis bases.

[1] S. M. Ibrahim Al-Rafia, M.R. Momeni, R. McDonald, M.J. Ferguson, A. Brown and E. Rivard, *Angewandte Chemie* **52**, 6390 (2013).
[2] NBO Version 3.1, Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F.
[3] S. M. Ibrahim Al-Rafia, M.R. Momeni, M.J. Ferguson, R. McDonald, A. Brown and E. Rivard, *Organometallics* **32**, 6658 (2013).
[4] Bader, R. F. W. Atoms in Molecules: A Quantum Theory. Oxford University Press: Oxford, 1990.



Superconvergent perturbation theory for intense-field quantum dynamics: From quasi-static to Floquet representations

Tung T. Nguyen-Dang
Département de chimie, Université Laval

Non-linear effects induced by an intense laser field in a molecule are often interpreted in terms of either of two pictures, thought to be distinct and complementary to one another, namely the quasi-static and the multiphoton or dressed-molecule pictures. We show that in fact the quasi-static picture emerges as the zero-frequency limit of the Floquet or dressed molecule representation. For low, but finite, non-zero frequency, non-adiabatic corrections to this zero-frequency Floquet representation can be obtained by applying superconvergent perturbation techniques, yielding rapidly successive higher-order adiabatic representations of the Floquet states. We illustrate the procedure on three classes of time-dependent, laser-driven systems, namely a linearly driven harmonic oscillator, a two-level (atomic) system, and a two-channel molecular system. In particular, we show how the infinite, periodic Floquet spectrum, defined at a finite value of the frequency, can be constructed out of the (time-parametrized) energy spectrum of the instantaneous Hamiltonian, and explore conceptual consequences of this construction.

Solvation of a poly(ethylene glycol) in aqueous droplets

Myong In Oh and Styliani Consta
Department of Chemistry, University of Western Ontario

Macromolecules in droplets are ubiquitous and commonly found in various settings such as atmospheric aerosols, ink-jet printing, and electrospray ionization mass spectrometry. Although they have been extensively studied by experiments, the macromolecule-solvent and macromolecule-ion interactions are not well understood at the atomistic level due to the complex nature of the interactions. In this study, a poly(ethylene glycol) (PEG) is solvated in different aqueous droplet environments. The behaviour of the macromolecule is investigated using constant-temperature molecular dynamics simulations and atomistic models where every atomic site is explicitly represented so that one can monitor various interactions explicitly.

Selectivity of alkali ions toward N, O, and S-containing ligands

Esam Orabi and Guillaume Lamoureux
Centre for Research in Molecular Modeling (CERMM)
and Department of Chemistry and Biochemistry, Concordia University

Inorganic cations are ubiquitous in biological systems. Metal ions contribute to biological function as counter ions, as triggers to cellular response, and as catalytic cofactors. They play structural roles such as Zn^{2+} in zinc-finger proteins and are part of the catalytic active site of metalloenzymes. Developing molecular models for ion-protein interactions is thus required to investigate and understand their various biological functions and to complement and interpret experimental data. For this purpose, polarizable potential models for NH_3 and H_2S, minimal model compounds of nitrogen and sulphur-containing amino acid side chains, are developed. The models are adjusted to reproduce the binding energies of the ligand's complexes with alkali ions (Li^+, Na^+, K^+, Rb^+, and Cs^+) calculated in gas phase using *ab initio* quantum chemistry methods. The models are used in molecular dynamics simulations to investigate the solvation structure and solvation free energy of alkali ions in pure NH_3 and H_2S and to investigate the preferential solvation of alkali ions in aqueous mixtures of the two solvents. Simulations of alkali ions in liquid NH_3 are showing solvation structures and solvation free energies in very good agreement with experimental results. Simulation of the ions in aqueous NH_3 and aqueous H_2S show that the ions are preferentially solvated by water in their first shell, consistent with the hard-soft acid-base theory. This indicates that alkali metal ions are expected to bind water (or any other O-containing ligand) rather than N- and S-containing ligands. The situation would likely be different for metal ions that are soft (such as Cd^{2+} and Pb^{2+}) or intermediate in hardness (such as Zn^{2+}). Simulating the selectivity of such metal ions is required for understanding the preferential coordination of metal ions in proteins.

Automated fit of high-dimensional potential energy surfaces

Slava Orel and René Fournier
Department of Chemistry, York University

We model the potential energy of molecules by a sum of energy contributions from each atom. These atomic energies depend on the local environment, ie, on the distribution of atoms around a given reference atom. The local environments are expressed by descriptors that are invariant to rotation and atom exchange. A database of hundreds to a few thousands of molecular geometries and the corresponding Density Functional Theory (DFT) energies is generated. The local atomic environments of the database are condensed into a set of representative configurations (atom types) by data clustering. Energies of these atom types are obtained by linear least-squares fit to the DFT molecular energies. To calculate the energy of a new molecular geometry, we perform interpolation in the space of descriptors to express each atom as a linear combination of atom types: we then take a weighted sum of atom type energies. The algorithm is almost completely automated and allows for energy calculations 1000-10,000 times faster than DFT while providing an accuracy of 1-3% for cohesive energies of metallic clusters of ~20 atoms. The algorithm shows promise for hybrid global optimization searches as it makes it possible to carry out thousands of energy evaluations based on a set of only a few hundred DFT-based energies.

Centroid dynamics with topological constraints

Lindsay A. Orr and Pierre-Nicholas Roy
Department of Chemistry, University of Waterloo

Real time simulation of quantum systems is known to be a computationally difficult task. Centroid quantum statistical mechanics, based on the Feynman path integral, is a classical-like formulation of quantum systems amenable to the calculation of time dependent statistical quantities. Reformulating the centroid approach using operators allows one to determine the classical-like symbol for a physical observable in the centroid phase space and is the most recent theoretical advancement of this method. So far only rectilinear motion has been cast using this theory; our goal is the theoretical development of the centroid operator approach for rotational motion using topological constraints on the quantised system. The particle on a ring is currently being investigated, with plans to extend the method to the particle on a sphere and the various rotating tops. Real time quantum correlation functions are to be computed for some simple test systems as proofs of concept using the approximate computational method known as centroid molecular dynamics. This will provide a connection to physical properties such as rotational spectra, transport properties, and chemical kinetics.

Exchange-correlation functionals for non-covalent interactions

Alberto Otero de la Roza[1], Erin R. Johnson[2] and Gino A. DiLabio[1]
[1]National Institute for Nanotechnology, National Research Council;
[2]Chemistry and Chemical Biology, University of California, Merced

Dispersion, an essential component of non-covalent interactions, is a long-range correlation effect. The non-covalent binding energies calculated using common density functionals vary widely from overly repulsive to spuriously attractive, and there is no a priori clear recipe for choosing any particular functional. Dispersion in DFT is, as a consequence, as much about calculating the dispersion energy accurately as it is about using a base density functional that gives the correct repulsive wall for all interaction types. In the context of pairwise dispersion corrections, this has been addressed by (over)using the dispersion damping function. In this talk, I present a study on the adequacy of different exchange and correlation approximations for non-covalent interactions as well as an analysis of the energy error scaling with system size. I will show, for instance, that cooperative effects in densely hydrogen-bonded systems (e.g. ice) are consistently overestimated by all density-functional approximations. Our results are relevant regarding the accuracy of molecular dynamics simulations, molecular crystal phase transitions, the scaling of non-covalent interactions to systems of biological interest, and the design of new base functionals for non-covalent interactions.

Theoretical and experimental investigations of the surface chemistry of nanodiamond

Jeffrey T. Paci[1], Han B. Man[2], Biswajit Saha[3], Dean Ho[4] and George C. Schatz[5]
[1]Department of Chemistry, University of Victoria and Northwestern University;
[2]Department of Mechanical Engineering, Northwestern University;
[3]School of Dentistry, UCLA;
[4]Department of Bioengineering, University of California;
[5]Department of Chemistry, Northwestern University

Nanodiamond has become an attractive option for a wide range of applications, including the delivery of genes and therapeutic drugs. Evidence suggests a high level of bio-compatibility, with the diamonds harmlessly flushed from human cells after the release of their payloads. Modest changes in salinity or pH can be enough to trigger binding or release. What are the processes responsible for these behaviors? We use a combined theoretical and experimental approach to explore the surface chemistry involved in binding and release. The surfaces of the nanodiamonds used in this study are graphitized, i.e., the nanodiamonds are types of buckydiamonds. The graphitization is thought to result from the harsh conditions used in the manufacture of the diamonds. These conditions also appear to result in a wide variety of functional groups on the surfaces. Elemental analysis, titration experiments, FT-IR and quantum mechanical modeling, provide extensive insight into the surface chemistry. Combined, these techniques are a means by which quantitative estimates of the concentrations of the various functional groups involved in binding and release from nanodiamonds can be made, and they provide insight into the mechanisms that govern the observed behaviors.

Chiral self-assembly at a solid surface: Complexity, models and mechanisms

Irina Paci, Tatiana Popa and Elvis Ting
Department of Chemistry, University of Victoria

In the bottom-up approach to nanotechnology, molecular-scale devices are constructed by designing their components to self-assemble and realize a desired structure or complex. In this context, the self-assembly process often occurs in the vicinity of a solid substrate. Theoretical investigations of surface self-assembly can be extremely useful counterparts to experimental studies, but can be challenging to pursue. One main issue is that while ultimately, quantum level information about the molecules, the surface and their interactions is essential to understand, the representative size of the system is more amenable to bulk simulations. This presentation will describe some of our group's efforts to advance the theoretical understanding of molecular self-assembly and behaviour on solid surfaces. Our studies of chiral structure formation at adsorption and its relationship to molecular structure will be discussed in some detail, with emphasis on both model molecules and small chiral aminoacids.

Evaluation of structural dynamics of different oligomers of glyceraldehyde-3-phosphate dehydrogenase (GAPDH)

Vinod Parmar, Gilles H. Peslherbe and Ann M. English
Centre for Research in Molecular Modeling (CERMM)
and Department of Chemistry and Biochemistry, Concordia University

The functions of glyceraldehyde-3-phosphate dehydrogenase (GAPDH) depend on its oligomeric state. For example, GAPDH exhibits dehydrogenase activity in the tetrameric state whereas monomeric nuclear GAPDH is implicated in DNA repair. The monomers and dimers of GAPDH are further implicated in the aggregation that contributes to neurodegeneration, including Alzheimer's disease. Cellular compartmentalization of GAPDH is also dependent on its oligomeric state. Alignment of monomers from the crystal structure of the GAPDH homotetramer does not reveal any significant differences so molecular dynamics simulations are being used to investigate the differences in dynamics of the protein oligomers. We find that the monomer is more flexible than the dimer and tetramer, which retain an overall structure close to the crystal structure with RMSD of 2 Å. The 25-residue S-loop, which is located at the tetramer interface and covers the active site, contributes to high RMSD of monomeric GAPDH. This loop has an average RMSD of 12 Å after 50 ns in the monomer vs 4 Å and 2 Å in the dimer and tetramer, respectively. In monomeric GAPDH the S-loop swings open and exposes the active site, which allows the NAD^+ cofactor to adopt an open conformation with its nicotinamide ring solvent exposed although the adenine group remains in its binding pocket. In contrast, NAD^+ has a binding pose close to that in the crystal structure in dimeric and tetrameric GAPDH. Differences in the structural dynamics of the S-loop suggest that it plays a key role in the formation of the various GAPDH oligomers.

How silver iodide particles nucleate ice

Grenfell Patey, Stephen Zielke and Allan Bertram
University of British Columbia

Water does not freeze homogeneously until -38 ^{o}C, therefore, freezing at higher temperatures relies on heterogeneous nucleation by foreign particles. This is important in the Earth's atmosphere, and much work has been done to identify which aerosols nucleate ice, and at what temperatures they are effective. However, why some aerosols function as ice nuclei while others do not is not well understood at the microscopic level. We report simulations of the nucleation and growth of bulk ice on several faces of silver iodide, which is a very effective ice nucleating agent. The simulations provide valuable insight into why silver iodide particles are such effective ice nuclei, and allow evaluation of previous ideas and theories concerning the physical characteristics of good ice nuclei.

Exact exchange based correlation energy functional designed from first principles

Jana Přecechtělová[1], Hilke Bahmann[1], Martin Kaupp[1] and Matthias Ernzerhof[2]
[1]Institut für Chemie, Technische Universität Berlin;
[2]Département de Chimie, Université de Montréal

Recent developments of density functional approximations focus on the design of exchange-correlation functionals that employ exactly computed exchange. The possibility to construct such a functional has been doubted in the literature [1] and identified as one of the outstanding problems in the contemporary DFT [2]. Previous attempts to develop the functional with standard approaches have not been successful and it remained a big unknown whether or not one could reach the goal with the so-called correlation factor (CF) model. We are pleased to answer these open questions and present the first empirical-parameter-free XC-functional that employs exact exchange and is based on the aforementioned model. The construction of the model has been pursued only sparsely before. We make it work for the first time ever for systems of chemical interest.

The CF model obtains the XC energy per electron from the XC hole approximated as a product of an exchange hole and a correlation factor [3]. First, we apply the Becke-Roussel model [4] to design an exchange hole reproducing the exact exchange energy per electron. Second, a matching correlation factor is constructed that transforms the exchange hole into an exchange-correlation hole. We propose a simple five-parameter ansatz for the CF and determine all parameters of the correlation factor model exclusively through exact constraints. This leads to an accurate completely nonempirical correlation energy functional that, in combination with exact exchange, shows a very promising performance for thermochemistry and kinetics. Provided that the exchange hole is normalized, the proposed correlation factor model becomes exact in the high-density limit, where exchange dominates correlation.

This research was supported by a Marie Curie International Outgoing Fellowship within the 7th European Community Framework Programme and by the Natural Sciences and Engineering Research Council of Canada.

[1] J. P. Perdew, V. N. Staroverov, J. Tao, G. E. Scuseria, *Phys. Rev. A,* **78**, 052513 (2008).
[2] A. Ruzsinszky, J. P. Perdew, *Comput. Theor. Chemistry,* **963**, 2 (2011).
[3] H. Bahmann, M. Ernzerhof, *J. Chem. Phys.,* **128**, 234104 (2008).
[4] A. D. Becke, M. R. Roussel, *Phys. Rev. A,* **39**, 3761 (1989).

A localized pair model of the chemical bond and non-covalent interactions

Jason K. Pearson, Brendan H. Sheppard, Adam J. Proud and Dylan C. Hennessey
Department of Chemistry, University of Prince Edward Island

The localized pair model [1] offers new and unique insight into electron-electron interactions present within the chemically intuitive, localized features of electronic structure. By calculating the electron pair distribution functions for the interelectronic separation (intracule), and center-of-mass (extracule) coordinates of localized molecular orbitals, one can characterize and quantify interactions within chemical systems. We have explored the application of intracule and extracule densities in both position and momentum spaces and find that interaction strengths are well correlated to either. Our results are consistent across a wide variety of chemical systems including covalent bonds, dative bonds and non-covalent interactions. In this talk, I will summarize our interest in the prediction of electronic pair distributions including the analysis of electronic structure [2,3], the interpretation of correlation effects [2,3,4] and the calculation of the correlation energy [5]. I will also highlight the capabilities of the localized pair model to characterize the chemical bond as well as non-covalent interactions, particularly hydrogen bonding.

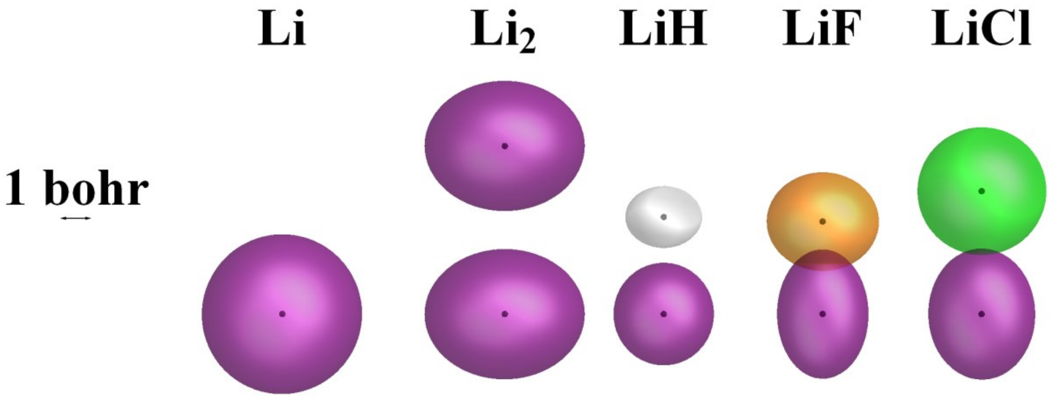
[1] Z. Zielinski and J.K. Pearson, *Comp. Theor. Chem.* **1003**, 79 (2013).
[2] A.J. Proud and J.K. Pearson, *J. Chem. Phys.* **133**, 134113 (2010).
[3] A.J. Proud and J.K. Pearson, *Chem. Phys. Lett.* **118**, 519, (2012).
[4] J.K. Pearson, P.M.W. Gill, J.M. Ugalde and R.J. Boyd, *Mol. Phys.* **107**, 1089 (2009).
[5] J.K. Pearson, D.L. Crittenden and P.M.W. Gill, *J. Chem. Phys.* **130**, 164110 (2009).

The Theory of Atoms and Bonds in Molecules from Radial Density

Raymond Poirier, Jessica Besaw and Peter Warburton
Memorial University

A novel method for defining Atoms and Bonds in Molecules (ABIM) has recently been developed through employment of radial electron density [1]. This concept is motivated by the radial distribution function of atoms which is well-known to partition an atom into shells, where each shell contains a realistic number of electrons. Similarly, procuring a realistic molecular radial density function enables the partitioning of molecules into core, bonding and non-bonding regions, while providing insight into the distribution of electron density. This poster will explore how the radial electron density of molecules can facilitate molecular partitioning, as well as discuss molecular radial density topology and the properties of atoms in molecules (AIMs). The figure shows the average shape of a Li atom and Li AIMs in various molecules.

[1] P.L. Warburton, R.A. Poirier, D. Nippard, *J. Phys. Chem. A.*, **115**, 852 (2011).



Extension of the source-sink potential (SSP) approach to multichannel quantum transport

Philippe Rocheleau and Matthias Ernzerhof
Département de Chimie, Université de Montréal

In molecular electronics, molecules are connected to macroscopic contacts and the current passing through is studied as a function of the applied voltage. We focus on modeling the transmission of π electrons through such a molecular electronic device (MED). Based on a simple Hückel Hamiltonian to describe the electrons in conjugated systems, the SSP method [1,2] employs complex potentials to replace the wavefunction of the infinite contacts in a rigorous way. The initial SSP approach was limited to one-dimensional contacts, here we extend the approach to multiple channels [3], i.e., to two-dimensional contacts including transverse modes. We describe the development of the method and illustrate it with applications within the Hückel approximation for π electrons.

[1] F. Goyer, M. Ernzerhof and M. Zhuang, *J. Chem. Phys.*, **126,** 144104 (2007).
[2] M. Ernzerhof, *J. Chem. Phys.*, **127**, 204709 (2007).
[3] P. Rocheleau, M. Ernzerhof, *J. Chem. Phys.*, **137**, 174112 (2012).

When and how does the geometric phase affect non-adiabatic excited-state dynamics through conical intersections?

Ilya G. Ryabinkin, Loic Joubert-Doriol and Artur F. Izmaylov
Department of Physical and Environmental Sciences, University of Toronto Scarborough

The adiabatic representation provides a natural framework for fully quantum simulations of non-adiabatic processes with on-the-fly evaluation of electronic surfaces and non-adiabatic couplings. However, in the presence of conical intersections (CIs) between electronic surfaces the adiabatic wave-functions acquire the geometric phase (GP) that can significantly change course of nuclear dynamics. In this work we are addressing questions when and how the GP affects the non-adiabatic dynamics. Our analysis is based on a local consideration of a linear vibronic coupling model Hamiltonian near the CI. We found that the GP role is twofold: First, it compensates for a repulsion created by the so-called diagonal Born—Oppenheimer correction and second, it enhances the non-adiabatic transition probability for a wave-packet part that experiences a central collision with the CI. To assess the significance of both GP contributions we have proposed two indicators that can be computed from parameters of electronic surfaces and initial conditions. Using examples of the bis(methylene) adamantyl and butatriene cations, and the pyrazine molecule we have demonstrated that the introduced indicators are very reliable in their predictions.

Inclusion of trial functions in the Langevin equation path integral ground state method: Application to parahydrogen clusters and their isotopologues

Matthew Schmidt, Steve Constable, Christopher Ing and Pierre-Nicholas Roy
Department of Chemistry, University of Waterloo

We develop and study the implementation of trial wavefunctions in the newly proposed Langevin equation Path Integral Ground State (LePIGS) method [*J. Phys. Chem. A* **117**, 7461 (2013)]. The LePIGS method is based on the Path Integral Ground State (PIGS) formalism combined with Path Integral Molecular Dynamics (PIMD) sampling using a Langevin equation based sampling of the canonical distribution. This LePIGS method originally incorporated a trivial trial wavefunction equal to unity. We now assess the effectiveness of three different trial wavefunctions on three isotopes of hydrogen for cluster sizes N = 4, 8, and 13. The trial wavefunctions of interest are the unity trial wavefunction used in the original LePIGS work, a Jastrow trial wavefunction that includes correlations due to hard-core repulsions, and a normal mode trial wavefunction that includes information on the equilibrium geometry. Based on this analysis, we opt for the Jastrow wavefunction to calculate energetic and structural properties for parahydrogen, orthodeuterium, and paratritium clusters of size N = 4 − 19, 33. Energetic and structural properties are obtained and compared to earlier work based on Monte Carlo PIGS simulations to study the accuracy of the proposed approach. The new results for paratritium clusters will serve as benchmark for future studies. Overall, we provide a detailed, yet general method for optimizing the necessary parameters required for the study of the ground state of a large variety of systems.

Time-resolved photoelectron spectra of wave packets across conical intersections in CS_2

Michael S. Schuurman[1], **Paul Hockett**[1] **and Vincent McKoy**[2]
[1]National Research Council of Canada;
[2]Department of Chemistry, California Institute of Technology

We report results from a novel fully *ab initio* method for simulating the time-resolved molecular-frame photoelectron angular distributions around conical intersections in CS_2. The technique employs wave packet densities obtained with the multiple spawning method in conjunction with geometry- and energy-dependent photoionization matrix elements. The robust agreement of these results with experimentally measured molecular-frame photoelectron angular distributions for CS_2 at various photoelectron kinetic energies demonstrates that this approach can successfully illuminate, and disentangle, the underlying nuclear and photoionization dynamics around conical intersections in polyatomic molecules.

Standard vs temperature-controlled locally enhanced sampling molecular dynamics simulations: O_2 diffusion in myoglobin as a case study

Maria S. Shadrina, Ann M. English and Gilles H. Peslherbe
Centre for Research in Molecular Modeling (CERMM)
and Department of Chemistry and Biochemistry, Concordia University

Small gas molecules play an important role in the function of many proteins. However, experimental studies of gas migration between their binding sites and the surface of the proteins are not straight forward and benefit from the insight provided by computer modeling. Standard molecular dynamics (MD) simulations can map gas diffusion within polypeptides but they require considerable computational time and resources even for small proteins. To facilitate studies of gas diffusion in proteins, we recently optimized MD simulation protocols that make use of temperature-controlled locally enhanced sampling (TLES) [1] and Langevin dynamics with a low damping coefficient (typically γ=0.5 ps^{-1}) [2]. The TLES method provides multiple diffusion trajectories per simulation by simulating the independent diffusion of multiple non-interacting copies of the gas molecule while the protein and water molecules experience the average interactions from all copies. Furthermore, the TLES method allows the effective temperature of the gas molecules to be raised, accelerating inter-cavity transition rates without altering the protein dynamics.

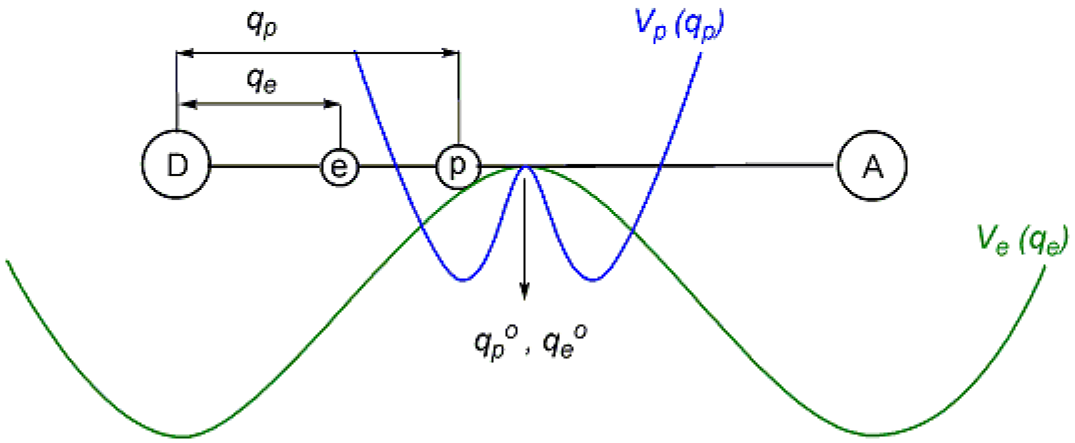
In the present work, we compare results obtained in standard and TLES MD simulations of O_2 diffusion in myoglobin (Mb). This is a monomeric protein found in muscle tissues that binds O_2 at its heme prosthetic group and quickly releases it on demand. Before escaping from Mb, O_2 placed in the distal heme cavity diffuses for ~100 ns within an extensive network of hydrophobic tunnels in the protein [3]. This requires highly computationally intensive standard MD simulations whereas the TLES approach provides similar results with a computational cost that is over two orders of magnitude lower. Hence the efficiency of the TLES method makes it suitable for rapidly mapping gas diffusion within proteins.

[1] J. Cohen, K. Kim, P. King, M. Seibert, K. Schulten, *Structure*, **13**, 1321 (2005).
[2] M. S. Shadrina, A. M. English, G. H. Peslherbe, *J. Am. Chem. Soc.*, **134**, 11177 (2012).
[3] J. Z. Ruscio, D. Kumar, M. Shukla, M. G. Prisant, T. M. Murali, A. V. Onufriev, *Proc. Natl. Acad. Sci. U. S. A.*, **105**, 9204 (2008).

An analysis of model proton-coupled electron transfer reactions via the mixed quantum-classical Liouville approach

Farnaz A. Shakib and Gabriel Hanna
Department of Chemistry, University of Alberta

The nonadiabatic dynamics of model proton-coupled electron transfer (PCET) reactions is investigated for the first time using a surface-hopping algorithm based on the solution of the mixed quantum-classical Liouville equation (QCLE). This method provides a rigorous treatment of quantum coherence/decoherence effects in mixed quantum-classical dynamics through evolution on both single adiabatic surfaces and on coherently coupled pairs of adiabatic surfaces, which is lacking in the molecular dynamics with quantum transitions (MDQT) surface-hopping approach commonly used for simulating PCET reactions. We apply the QCLE approach to a minimal model consisting of a proton and an electron, which are treated quantum mechanically, and a single solvent coordinate, which is treated classically. Both concerted and sequential PCETs are studied for a wide range of couplings between the proton/electron and the solvent, and insights into the dynamical principles underlying these reactions are gained. Notably, an examination of the reactive trajectories in all cases reveals that the system spends the majority of its time on the average of two coherently coupled adiabatic surfaces. The results of this study demonstrate the applicability of QCLE-based surface-hopping dynamics to the study of a wide range of model PCET reactions and, therefore, could form the basis for future investigations of PCET in more complex systems.



Reaction-specific semiempirical models for proton transfer reactions in aqueous solution

Bharat Kumar Sharma[1,2]**, Shihao Wang**[1] **and Guillaume Lamoureux**[1]
[1]Department of Physics, Concordia University;
[2]Centre for Research in Molecular Modeling (CERMM)
and Department of Chemistry and Biochemistry, Concordia University

Because of their computational cost, applications of high-level quantum mechanical methods are limited to small to medium sized molecular systems. Semiempirical methods based on the neglect of diatomic differential overlap (NDDO) approximation represent an acceptable computational cost even for relatively large systems, provided they are tailored to reproduce the physical and chemical properties of interest. The standard semiempirical AM1 model is reparameterized for the purpose of describing the structure of bulk water and the structure and energetics of proton transfer reactions in water. Semiempirical parameters are optimized for H and O using a genetic algorithm approach to reproduce geometries and energies (deprotonation, hydrogen bonding, proton transfer, reaction, and activation energies) of a set of compounds (the training set) calculated from density functional theory (DFT). The training set contains water monomer, dimer, and trimer in their neutral, protonated, and deprotonated forms. The transferability of the model is assessed for a large testing set of water tetramers, pentamers, and hexamers. The optimized model provides a significant improvement over existing semiempirical models. In molecular dynamics simulations of bulk water, it yields a liquid structure in agreement with experimental data. The model is further used to calculate pKa shifts of zinc-bound ligands (water and hydrogen sulfide) in aqueous solution. The parameterization procedure is aimed at developing reaction-specific semiempirical models to elucidate ligand exchange and reactivity in metalloenzymes.

Electron transport in nanoscale junctions with local anharmonic modes

Lena Simine and Dvira Segal
Department of Chemistry, University of Toronto

We study electron transport in nanojunctions in which an electron on a quantum dot or a molecule is interacting with an N-state local impurity, a harmonic (Holstein) mode, or a two-state system (spin). These two models, the Anderson-Holstein model and the spin-fermion model, can be conveniently transformed by a shift transformation into a form suitable for a perturbative expansion in the tunneling matrix element. We explore the current-voltage characteristics of the two models in the limit of high temperature and weak electron-metal coupling using a kinetic rate equation formalism, considering both the case of an equilibrated impurity, and the unequilibrated case. Specifically, we show that the analog of the Franck-Condon blockade physics is missing in the spin-fermion model. We complement this study by considering the low-temperature quantum adiabatic limit of the dissipative spin-fermion model, with fast tunneling electrons and a slow impurity. While a mean-field analysis of the Anderson-Holstein model suggests that nonlinear functionalities, bistability and hysteresis may develop, such effects are missing in the spin-fermion model at the mean-field level.

The multi-reference nature of chemistry from geminals

Pawel P. Tecmer[1], Katharina K. Boguslawski[1], Paul W. Ayers[1] and Dimitri D. Van Neck[2]
[1]Department of Chemistry and Chemical Biology, McMaster University;
[2]Center for Molecular Modelling, Ghent University

The accurate description of the electron-electron interaction is a key problem in quantum chemistry and condensed matter physics. While there exists a number of efficient algorithms to account for the weak (dynamic) electron correlation energy (e.g. perturbation or coupled cluster theories), the description of strong (nondynamic and static) correlation effects is more difficult and is usually associated with a factorial growth of computational expenses.

In this work, we present an efficient approach to the electron correlation problem that is well suited for strongly interacting many-body systems, but requires only mean-field-like computational cost. Our method uses geminals (two-electron basis functions) as building blocks for the wave function [1]. In particular, we focus on the antisymmetric product of 1-reference-orbital geminals (AP1roG) [2] model that, combined with a variational orbital optimization protocol (vOO-AP1roG) [3] provides a promising size-extensive and size-consistent alternative to the standard correlation methods.

The performance of our approach is assessed against one-dimensional Hubbard rings with different numbers of sites, for the symmetric dissociation of the H_{50} hydrogen chain and spectroscopic constants of some diatomic molecules [3,4].

[1] P. R. Surjan, A. Szabados, P. Jeszenszki, and T. Zoboki, *J. Math. Chem.* **50**, 534 (2012).

[2] P. A. Limacher, P. W. Ayers, P. A. Johnson, S. De Baerdemacker, D. Van Neck, and P. Bultinck, *J. Chem. Theory Comput.* **9**, 1394 (2013).

[3] K. Boguslawski, P. Tecmer, P.W. Ayers, P. Bultinck, S. De Baerdemacker, D. Van Neck, *Phys. Rev. B* **89**, 201106(R) (2014).

[4] P. Tecmer, K. Boguslawski, P. A. Johnson, P. A. Limacher, Matthew Chan, Toon Verstraelen and P. W. Ayers (DOI: 10.1021/jp502127v).

Coarse-grained molecular dynamics simulations of protein complexes with charge hopping

Mark Thachuk and Sarah Fegan
Department of Chemistry, University of British Columbia

We have developed an algorithm for moving charges in coarse-grained molecular dynamics simulations of protein complexes. The goal of the current work is to study the importance of the N-terminus in the unfolding of the proteins, and to investigate the possibility of controlling the unfolding of protein complexes in the gas phase. In order to see the importance of the N-terminus, trajectories where the N-termini of all the monomers in the complex can be positively charged are compared with trajectories where only one monomer has the N-terminus as a basic site. To control the unfolding, we have added small tethers to one monomer in the complex. Each tether is a small group of beads with one or more basic sites. Increasing the number of basic sites will encourage the charge accumulation on that monomer, thus increasing the unfolding behaviour of that monomer relative to the rest of the complex.

High-dimensional quantum dynamics: compact storage of multidimensional wavefunctions using canonical polyadic (CP) tensor format

Phillip S. Thomas[1], Arnaud Leclerc[2] and Tucker Carrington[1]
[1]Department of Chemistry, Queen's University;
[2]Théorie-Modélisation-Simulation, Université de Lorraine

Quantum dynamics calculations on molecules and reacting systems are fundamentally important for modeling spectroscopy and chemical reaction dynamics. The primary limitation of quantum dynamical methods using the standard "direct-product" representation is that n^D components of the wavefunction must be explicitly stored (for D degrees-of-freedom (DOFs) and n basis functions-per-DOF). The exponential blow-up of storage is known as the "curse of dimensionality" and limits the standard method to molecules having no more than four atoms (6 vibrational DOFs).

Recent work suggests that tensor decomposition methods may be a way to alleviate the curse, enabling quantum dynamics on larger molecules. We recently computed energy levels for a model system having 20 vibrational DOFs using canonical polyadic (CP) tensor format to store the wavefunction. The CP-format requires storing only r*n*D components, which is much less than n^D as long as the rank r can be kept small. In this work we explore strategies for managing the rank in a practical calculation. The first is to improve the alternating-least-squares rank-reduction algorithm used in the recent calculations. The second is to group highly-coupled DOFs using a "mode-combination" approach so that a large rank is not needed to represent important mode couplings.

Efficient model for cytochrome P450 aromatic oxidation

Anna Tomberg and Nicolas Moitessier
Department of Chemistry, McGill University

The ability to predict the formation of reactive metabolites during the metabolism of a drug would allow for a more efficient drug discovery process by identifying potentially toxic compounds at an earlier stage. Examples of such toxic molecules are epoxides, since they can covalently bind to macromolecules in the body. The formation of epoxides can arise from the oxidation of aromatic compounds by Cytochrome P450 (CYP) enzyme, commonly found in the liver. Using Density Functional Theory, we are modeling the catalytic site of CYPs and a set of small substrates in order to better understand their reactivity toward aromatic oxidation. The active species of CYPs is an iron-heme complex, which oxidizes substrates by a radical pathway. The different reaction mechanisms of oxidation and challenges in modelling this transition metal complex will be discussed.

Computational design of narrow-bandgap ZnO/ZnS layered heterostructures

Amin Torabi and Viktor N. Staroverov
Department of Chemistry, University of Western Ontario

Zinc oxide (ZnO) and zinc sulfide (ZnS) are abundant, chemically stable, nontoxic semiconductor materials. Unfortunately, the fundamental bandgaps of ZnO (Eg = 3.4 eV) and ZnS (Eg = 3.91 eV) are too large for these materials to be useful in light-harvesting applications. Using density-functional methods we show that the bandgaps of ZnO and ZnS can be dramatically reduced by creating layered ZnO/ZnS heterostructures. For instance, substitution of every tenth ZnS monolayer in the crystal structure of bulk zinc sulfide with a ZnO monolayer (9:1 ZnS to ZnO ratio) causes the bandgap to drop by about 1.5 eV. The bandgap further decreases with increasing ZnO content and reaches a minimum of Eg = 1.5 eV for the ZnO/ZnS heterostructure in which every 5 contiguous layers of ZnS alternate with 5 contiguous layers of ZnO (5:5 ratio). The predicted bandgap variations of ZnO/ZnS heterostructures span much of the visible region of the solar spectrum, which makes these materials well-suited for photovoltaic device engineering.

Spectral and dynamical effects on the vibrational distribution of H_2 after molecular ionization by a single XUV-attosecond pulse

Jérémy Viau-Trudel[1], T. Tung Nguyen-Dang[1] and Osman Atabek[2]
[1]Département de chimie, Université Laval;
[2]Institut des Sciences Moléculaires d'Orsay, CNRS

Molecular dissociative ionization pump-probe spectroscopic schemes, using an XUV-attosecond pump pulse (or pulse-train) and a few-cycle IR probe pulse, allows one to investigate the formation and subsequent dynamics of the ionic vibrational wavepacket. By monitoring the kinetic energy distribution of the dissociated fragments as a function of the time-delay between the pump and the probe pulses, a clear distinction between adiabatic and non-adiabatic transport regimes of field-induced vibrational resonances can be made [1,2]. Theoretical interpretation and numerical simulations of this type of experiment generally assumed that the ionization process is a vertical transition according to the celebrated Franck-Condon principle. In this work, we compare the sudden approximation underlying this Franck-Condon principle with a complete description of the field induced multi-electron dynamics [3] leading to the ionization of H_2 by a single XUV-attosecond laser pulse. Despite the fact that the ionization probability evaluated at a fixed nuclear geometry is correctly captured by the sudden approximation, significant deviations from the Franck-Condon profile are observed in the vibrational distributions of H_2 produced after the strong-field ionization. We discuss how these deviations depend on the fast multi-electron dynamics and show that both the frequency and duration of the ionizing pulse can have a strong effect on the molecular-geometry-dependent phase of the wave function.

[1] F. Kelkensberg et al., *Phys. Rev. Lett.*, **103**, 123005 (2009).
[2] C. Lefebvre et al., *Phys. Rev. A*, **88**, 053416 (2013).
[3] T. T. Nguyen-Dang and J. Viau-Trudel, *J. Chem. Phys.*, **139**, 244102 (2013).

Quantum monte carlo simulation of vibrational frequency shifts of CO in solid para-hydrogen

Lecheng Wang, Robert J. Le Roy and Pierre-Nicholas Roy
Department of Chemistry, University of Waterloo

Stimulated by the experimental rovibrational spectroscopic measurements of CO isotopologues isolated in solid para-hydrogen [1], the current quantum Monte Carlo simulations were carried out to provide some quantum mechanical insights into the experimental observations. Using path integral Monte Carlo (PIMC) with periodic boundary conditions, we first generated and optimized both the fcc and hcp structures of pure solid para-hydrogen based on the recently developed H_2-H_2 potential [2]. Then the substitution site of a CO molecule in solid para-hydrogen was investigated using Monte Carlo sampling, and the structural and dynamical behaviors of the micro-solvation environment around CO were simulated via PIMC. The recently reported H_2-CO potentials [3] were used to depict the intermolecular interaction of H_2-CO. The effective rotational constants of CO in different solid para-hydrogen structures were also theoretically calculated and were compared with the experimental observations, as well as reported values in large-sized para-hydrogen-CO clusters [4].

[1] M. E. Fajardo, *J. Phys. Chem. A* **117**, 13504 (2013).
[2] N. Faruk and co-workers, submitted (2014).
[3] H. Li and co-workers, *J. Chem. Phys.* **139**, 164315 (2013).
[4] Y. Mizumoto and Y. OhtsukiChem. *Phys. Lett.* **501**, 304 (2011).

An accurate potential energy surface for methane

Xiaogang Wang and Tucker Carrington
Department of Chemistry, Queen's University

We obtain an accurate methane PES by starting with the *ab initio* PES of Schwenke and Partridge [*Spectrochim. Acta A* **57**, 887 (2001)] and adjusting 5 of their parameters to reproduce 40 reliable vibrational levels of CH_4. The fit reduces the root mean squares deviation (RMSD) from 4.80 cm^{-1} to 0.28 cm^{-1}. Since not all of the Tetradecad levels are certain, only 5, those confirmed by direct experimental transitions, are included in the fit. The new PES ought therefore to aid in the analysis of the Tetradecad polyad. To further test the accuracy of the new PES, vibrational levels are computed for CH_4, CH_3D, CHD_3, CH_2D_2 and $^{13}CH_4$ and are compared with the extensive experimental data. The errors are all within about one cm^{-1} except for a few cases.

Systematic construction of models for the exchange hole of density functional theory

Rodrigo Wang and Matthias Ernzerhof
Département de Chimie, Université de Montréal

To further improve Kohn-Sham density functional theory better functionals for the exchange-correlation energy have to be developed. Here, we focus on exchange functionals that are responsible for most of the errors of exchange-correlation energy functionals. We develop new models for the exchange hole that are suitable to describe delocalized holes. The key ingredient in these models is the Taylor series expansion of the exchange hole in terms of the electron-electron distance. With our new hole models, we reproduce this expansion up to fourth order. This extends on existing approximations that reproduce the series expansion only to second order. The implementation of the fourth order Taylor series expansion into the Gaussian Program is described.

Computer Simulations of the Vibrational Spectra of Ion-Water Clusters: The OH Stretch as a Signature of Water Binding

Xijun Wang and Gilles H. Peslherbe
Centre for Research in Molecular Modeling (CERMM)
and Department of Chemistry and Biochemistry, Concordia University

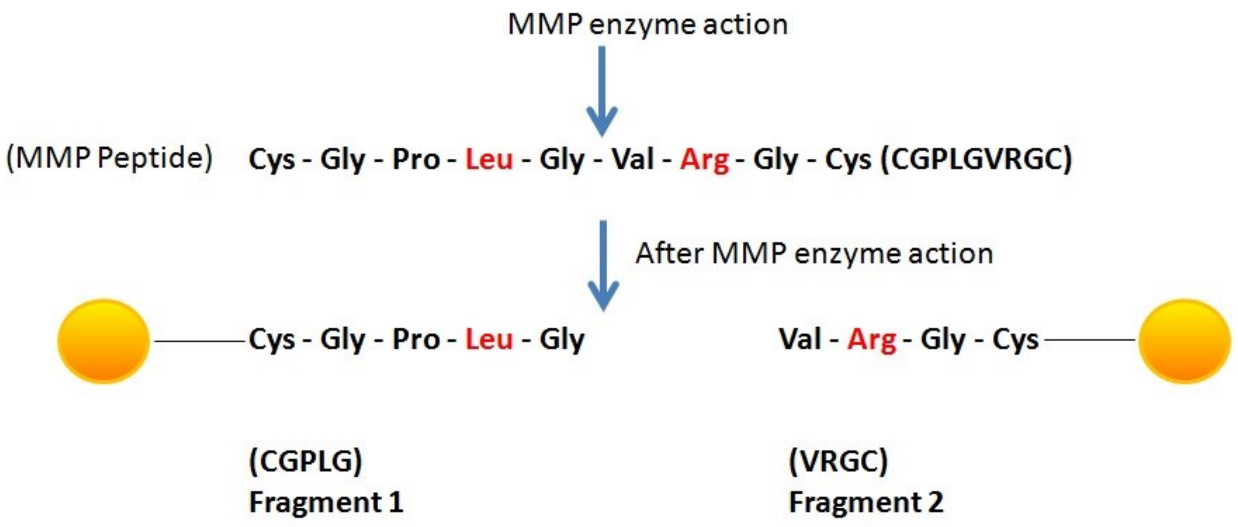
Infrared spectroscopy is increasingly employed to attempt to probe the structure and conformational dynamics of ion-water clusters, and the OH bond stretch is often taken as a signature of the binding state of water in the clusters. To build a connection between observed spectra and cluster structure and vibrational dynamics, molecular dynamics simulations based on approximate density-functional theory are performed to simulate infrared spectra of sulfate-water clusters as a case study. Vibrational spectra are calculated as the Fourier transform of the autocorrelation function of the dipole moment of the cluster or a given molecule within the cluster. The decomposition and band assignment of the simulated spectra is achieved by comparison of the vibrational power spectra of individual water molecules in different binding states. The cluster size dependence of the OH stretch region and temperature effects are investigated. Simulated spectra are found to be reasonably consistent with experimental results. This work does not only improve our understanding of experimental vibrational spectra, but also provides a validation of our methodology to describe the vibrational dynamics of ion-water clusters.

Theoretical PM6 study of the MMP peptide
Au-Cys - Gly - Pro - Leu - Gly - Val - Arg - Gly - Cys-Au

Michael A. (Tony) Whitehead[1], Ashok Kakkar[1], Promad Avti[2],
Dylan Baker[1] and Frederic Lesage[3]
[1]Department of Chemistry, McGill University;
[2]Biomedical Imaging, Ecole Polytechnique;
[3]Electrical Engineering, Ecole Polytechnique

During atherosclerosis progression, proteases, such as matrix metallo-proteinase (MMP) are expressed leading to the degradation of extra cellular matrix making the plaque vulnerable, leading to a heart attack. To detect the plaque vulnerability, in vivo, identifying the expression of MMP's is crucial. The use of a MMP recognising peptide sequence could be used as an imagining probe to identify the MMP expression using Au imaging atom. The calculation of MMP peptide (Au Cys - Gly - Pro - Leu - Gly - Val - Arg - Gly - Cys Au) and its results are compared to the MMP peptide with Au and Ag using bond lengths, dihedral angles, electrostatic surface potentials and de-localised molecular orbitals within the PM6 theory.

M . Swierczewska, S. Lee, X. Chen. *Phys. Chem. Chem. Phys.* **13**, 9929 (2011).



Influence of molecular size on the density-functional delocalization error

Sarah R. Whittleton[1], Robert A. Bailey[1], Alberto Otero-de-la-Roza[2] and Erin R. Johnson[1]
[1]Chemistry and Chemical Biology, University of California, Merced;
[2]National Institute for Nanotechnology, National Research Council of Canada

While density-functional theory is an effective and popular method in quantum chemistry, approximations within the exchange-correlation functional can produce substantial inaccuracies. For example, generalized-gradient approximation (GGA) functionals produce convex energy versus charge curves that violate the correct piecewise-linearity constraint of E(N) for fractional charges, referred to as delocalization error. This leads to a false description of molecular properties, such as the HOMO and LUMO energy levels. This work investigates the delocalization error in a series of gas-phase organic molecules, including alkanes, alkenes, oligoacenes, and ensembles of methane molecules. The GGA deviation from linearity of the E(N) curves is evaluated and ω-tuning of a long-range corrected functional is performed for each molecule/system. It is found that the deviation from linearity, and thus the optimal ω, decreases with increasing molecular size. However, systematic error in the endpoint of the E(N) curve, and thus in the ionization potential, is simultaneously introduced, demonstrating the impact of molecular size on delocalization error.

Quantum properties of confined systems

Spencer B. Yim and Pierre-Nicholas Roy
Department of Chemistry, University of Waterloo

This work presents an investigation on the quantum effects of confined systems, both in the ground state as well as at finite temperature. Simulations are conducted within the framework of the Molecular Modeling Toolkit (MMTK), an open source library written in Python [1]. Path integral molecular dynamics (PIMD) is used in order to capture the quantum results, with the path integral Langevin equation (PILE) being implemented as a thermostat [2]. The current system under scrutiny consists of a single water molecule that is encapsulated inside of a buckyball (H_2O@C60). This specific system has attracted much attention in the literature in recent years, with numerous studies on the nuclear spin and quantum rotation of the water [3]. An emphasis of this work is placed on the optimization of parameters including: number of beads and timestep, whose optimization was based on energy convergence studies, and the Langevin equation friction coefficient, which was optimized by looking at the autocorrelation function of several observables. The effort to retrieve properties such as energy, heat capacity, and various spectra is discussed.

[1] K. Hinsen*,* *J. Comput. Chem.* **21**, 79 (2000).
[2] M. Ceriotti, M. Parrinello, T. E. Markland, D. E. Manolopoulos, *J. Chem. Phys.* **133**, 124104 (2010).
[3] C. Beduz, M. Carravetta, J. Y. C. Chen, M. Concistrè, M. Denning, M. Frunzi, A. J. Horsewill, O. G. Johannessen, R. Lawler, X. Lei, M. H. Levitt, Y. Li, S. Mamone, Y. Murata, U. Nagel, T. Nishida, J. Ollivier, S. Rols, T. Rõõm, R. Sarkar, N. J. Turro, and Y. Yang. *PNAS* **109**, 12894 (2012).

Material informatics tools for aiding in the discovery of new metal organic frameworks (MOFs) for CO_2 scrubbing of natural gas

Mohammad Zein Aghaji, Peter Boyd, Tom Daff and Tom Woo
Department of Chemistry, University of Ottawa

Removing CO_2 from unconventional natural gas reservoirs is a vital step for natural gas purification. Recently metal organic frameworks (MOFs) have received considerable attention because of their potential in gas separation applications. MOF materials have many benefits over traditional zeolites because of their larger surface areas, pore volumes and functionality. However, designing MOFs with these optimal properties presents a remarkable challenge due to limitless combinations of metal nodes and organic linkers (building blocks). Newly the hypothetical-MOFs database was generated from 70 building blocks and 20 functional groups in our lab. With such a large database, first, we have screened ~320,000 structures from our in-house hypothetical MOF database under pressure swing adsorption conditions using Grand Canonical Monte Carlo simulation for CO_2 separation from CH_4. Computational high throughput screening provided a fairly large number of synthetic potential targets (2,000) which beat the popular commercial zeolite 13X. Afterword, we developed a novel web-based cheminformatics tool, MOFfinder, to enable synthesis chemists to find more synthesis targets from our database for natural gas purification via search of structural building blocks and adsorption properties just in few seconds. To find more MOFs of interest, all MOFs in our database were decomposed into their inorganic and organic SBUs. All functionalized organic SBUs were converted to their relative SMILES. With such a large library of SMILES (200,000), substructure and similarity searches can be performed.

Path integral with a Tsallis propagator

Dongbin Zhang
Department of Chemistry, University of Waterloo

The Feynman Path Integral formulation of Quantum Mechanics has provided a mechanism for modelling quantum systems through methods such as PIMD and PIMC. Our ability to model complex quantum systems is however limited by the computational complexity arising from the path integral formalism. This project seeks to reduce the computational difficulty by employing new and potentially more efficient formulations of the imaginary path integral problem. Our theories of new path integrals are based on Tsallis statistics, a direction first proposed by Straub [Chem Phys Lett, 346, 3-4, 274 (2001)]. So far we have been able to identify and validate a number of new Tsallis path integrals. Early results show that some of the variants consistently require fewer beads (time-sclices) for the same precision than the original path integral formalism, which means the computational complexity of path integrals can be significantly reduced. Permanent reduction on computational complexity will increase the scope of potential applications of the path integral formalism as a whole.

I. J. E. Andricioaei, K. M. Straub, *Chem. Phys. Lett.* **346**, 274 (2001).

Approximating the exchange energy through the non-empirical exchange factor approach

Yongxi Zhou, Helene Antaya and Matthias Ernzerhof
Department of chemistry, Université de Montréal

Various widely used approaches for the exchange-correlation energy of Kohn-Sham theory, such as the generalized gradient approximation and hybrid methods, suffer from the one-electron self-interaction error. This error manifests itself in one-electron or two-electron spin-unpolarised systems. We propose new approximations to the exchange energy that are exact for the aforementioned systems. Starting from the weighted density approximation (WDA), we introduce several weighting factors (that we refer to as exchange factors) which are designed to reproduce various properties of the exact exchange hole. Furthermore, a new exact condition for the exchange factor is presented that concerns the asymptotic behavior of the exchange hole as one electron coordinate moves out to infinity. Observance of this and other conditions results in exchange functionals that improve upon WDA.

List of participants

Mohamed Aboelnga	University of Windsor	aboelnga@uwindsor.ca
Carlo Adamo	Institut de Recherche Chimie Paris, CNRS	carlo.adamo@chimie-paristech.fr
Cesar Almora-Diaz	Universidad Nacional Autonoma de Mexico	xalmora@fisica.unam.mx
James Anderson	RIKEN	james.anderson@riken.jp
Philippe Archambault	Concordia University	p.archambault@concordia.ca
Gustavo Avila-Blanco	Queen's University	Gustavo.Avilla-Blanco@chem.queensu.ca
Hilke Bahmann	Technische Universität Berlin	hilke.bahmann@tu-berlin.de
André Bandrauk	Université de Sherbrooke	andre.bandrauk@usherbrooke.ca
Marc-André Bélanger	Université de Montréal	udem.marc.andre.belanger@gmail.com
Kevin Bishop	University of Waterloo	kpbishop@uwaterloo.ca
Shamus Blair	University of New Brunswick	shamus.a.blair@gmail.com
Éric Blanchette	Université Laval	eric.blanchette.4@ulaval.ca
Katharina Boguslawski	McMaster University	bogusl@mcmaster.ca
Russell Boyd	Dalhousie University	russell.boyd@dal.ca
James Brown	Queen's University	9jhb3@queensu.ca
Alex Brown	University of Alberta	alex.brown@ualberta.ca
Paul Brumer	University of Toronto	pbrumer@chem.utoronto.ca
Natalie Cann	Queen's University	natalie.cann@chem.queensu.ca
Tucker Carrington	Queen's University	tucker.carrington@queensu.ca
Mark Casida	Université Joseph Fourier (Grenoble I)	Mark.Casida@ujf-grenoble.fr
Yuzhe Chen	University of British Columbia	stanyuzhe@gmail.com
Guan Hua Chen	University of Hong Kong	ghc@everest.hku.hk
Young-Sang Cho	University of Waterloo	yscho88@hotmail.com
Cassandra Churchill	University of Alberta	churchil@ualberta.ca
David Clary	University of Oxford	david.clary@chem.ox.ac.uk
Cecilia Clementi	Rice University	cecilia@rice.edu
Sean Collins	University of Ottawa	scollin3@uottawa.ca
Kevin Conley	McGill University	kevin.conley@mail.mcgill.ca
Styliani Consta	University of Western Ontario	styliani.constas@gmail.com
Michel Côté	Université de Montréal	Michel.Cote@umontreal.ca
Rogelio Cuevas-Saavedra	University of Western Ontario	rcuevass@uwo.ca
Thomas Daff	University of Ottawa	tdaff@uottawa.ca
Stephen Dale	University of California Merced	sdale@ucmerced.edu
Clara del Junco	McGill University	clara.deljunco@gmail.com
Robert Doerksen	University of Mississippi	rjd@olemiss.edu
Allan East	University of Regina	allan.east@uregina.ca
Ann English	Concordia University	ann.english@concordia.ca
Matthias Ernzerhof	Université de Montréal	matthias.ernzerhof@umontreal.ca
Nabil Faruk	University of Waterloo	nffaruk@gmail.com
René Fournier	York University	renef@yorku.ca
Thomas Frauenheim	University of Bremen	frauenheim@bccms.uni-bremen.de
Mirza Galib	University of Alberta	mgalib@ualberta.ca
Miguel Angel Garcia Chavez	University of British Columbia	mgarcia@chem.ubc.ca
James Gauld	University of Windsor	gauld@uwindsor.ca
Xiaoxia Ge	Research Foundation of CUNY	xge2009@gmail.com

Melis Gedik	University of Alberta	mgedik@ualberta.ca
Andreas Görling	Friedrich-Alexander-Universität Erlangen-Nürnberg	Andreas.Goerling@chemie.uni-erlangen.de
Cristina Gonzalez	McMaster University	gonzalce@mcmaster.ca
Heather Gordon	Brock University	hgordon@brocku.ca
Stefan Grimme	Bonn University	grimme@thch.uni-bonn.de
Hong Guo	McGill University	guo@physics.mcgill.ca
Gabriel Hanna	University of Alberta	gabriel.hanna@ualberta.ca
Martin Head-Gordon	University of California Berkeley	m_headgordon@berkeley.edu
Kade Head-Marsden	McGill University	kheadmarsden@gmail.com
Salima Hennani	Université Laval	salima_hennani_2555@yahoo.fr
Joshua Hollett	University of Winnipeg	j.hollett@uwinnipeg.ca
Gerhard Hummer	Max Planck Institute of Biophysics	gerhard.hummer@biophys.mpg.de
Radu Iftimie	Université de Montréal	radu.ion.iftimie@umontreal.ca
Dmitri Iouchtchenko	University of Waterloo	diouchtc@uwaterloo.ca
Chiaki Ishibashi	Chiba Institute of Technology	s1379501UJ@s.chibakoudai.jp
Soran Jahangiri	Concordia University	soranjh@gmail.com
Benjamin Janesko	Texas Christian University	b.janesko@tcu.edu
Guangfu Ji	Institute of Fluid Physics	cyfjkf@126.com
Erin Johnson	University of California Merced	ejohnson29@ucmerced.edu
Loïc Joubert-Doriol	University of Toronto	loic.joubert.doriol@utoronto.ca
Raymond Kapral	University of Toronto	rkapral@chem.utoronto.ca
Martin Kaupp	Technische Universität Berlin	martin.kaupp@tu-berlin.de
Taewon Kim	McMaster University	kimt33@mcmaster.ca
Mariusz Klobukowski	University of Alberta	mariusz.klobukowski@ualberta.ca
Denise Koch	Concordia University	denise.koch@concordia.ca
Sviataslau Kohut	University of Western Ontario	skohut7@uwo.ca
Peter Kusalik	University of Calgary	pkusalik@ucalgary.ca
Branka Ladanyi	Colorado State University	bl@lamar.colostate.edu
Guillaume Lamoureux	Concordia University	guillaume.lamoureux@concordia.ca
Jin Lee	Thompson Rivers University	jinlee88@gmail.com
Sébastien Légaré	Université Laval	sebastien.legare.2@ulaval.ca
Joshua Littleton	University of Western Ontario	jlittlet@uwo.ca
Xingchen Liu	University of Calgary	xcliu.cn@gmail.com
zhaomin liu	McGill Chemistry	zhaomin.liu@mail.mcgill.ca
Neepa Maitra	Hunter College and Graduate Center of the City University of New York	nmaitra@hunter.cuny.edu
Chun Chi Mak	Concordia University	chunchi.mak@concordia.ca
Steven Maley	Lakehead University	smaley@lakeheadu.ca
Margot Mandy	University of Northern British Columbia	mandy@unbc.ca
Sergei Manzhos	National University of Singapore	mpemanzh@nus.edu.sg
Franz Martinez	University of Alberta	fmmartin@ualberta.ca
Hidenori Matsuzawa	Chiba Institute of Technology	hidenori.matsuzawa@it-chiba.ac.jp
Csongor Mátyás	Memorial University	cfm482@mun.ca
Robert Mawhinney	Lakehead University	rcm@lakeheadu.ca

Thomas Miller	California Institute of Technology	tfm@caltech.edu
Mohammad Reza Momeni Taheri	University of Alberta	momenita@ualberta.ca
Marcel Nooijen	University of Waterloo	nooijen@uwaterloo.ca
Myong In Oh	University of Western Ontario	moh22@uwo.ca
Esam Orabi	Concordia University	esam_oraby2001@yahoo.com
Slava Orel	York University	slavao@yorku.ca
Lindsay Orr	University of Waterloo	laorr@uwaterloo.ca
Alberto Otero de la Roza	National Institute for Nanotechnology, NRC	aoterodelaroza@ucmerced.edu
Jeffrey Paci	University of Victoria	jeffrey.paci@gmail.com
Irina Paci	University of Victoria	ipaci@uvic.ca
Vinodbhai Parmar	Concordia University	vinodniper3785@gmail.com
Grenfell Patey	University of British Columbia	patey@chem.ubc.ca
Jason Pearson	University of PEI	jpearson@upei.ca
Gilles Peslherbe	Concordia University	gilles.peslherbe@concordia.ca
Raymond Poirier	Memorial University	rpoirier@mun.ca
Alex Polgar	University of Western Ontario	apolgar5@uwo.ca
Regis Pomes	Hospital for Sick Children and University of Toronto	pomes@sickkids.ca
Jana Přecechtělová	Technische Universität Berlin	j.precechtelova@gmail.com
Mark Ratner	Northwestern University	ratner@northwestern.edu
Françoise Remacle	Université de Liège	FRemacle@ulg.ac.be
Philippe Richer	Université de Montréal	philippe.richer@umontreal.ca
Philippe Rocheleau	Université de Montréal	philippe.rocheleau2@gmail.com
Benoît Roux	University of Chicago	roux@uchicago.edu
Pierre-Nicholas Roy	University of Waterloo	pnroy@uwaterloo.ca
Ilya Ryabinkin	University of Toronto	i.ryabinkin@utoronto.ca
Dennis Salahub	University of Calgary	dennis.salahub@ucalgary.ca
H. Bernhard Schlegel	Wayne State University	hbs@chem.wayne.edu
Matthew Schmidt	University of Waterloo	mdgschmi@uwaterloo.ca
Jeremy Schofield	University of Toronto	jmschofi@chem.utoronto.ca
Michael Schuurman	National Research Council	Michael.Schuurman@nrc-cnrc.gc.ca
Dvira Segal	University of Toronto	dsegal@chem.utoronto.ca
Maria Shadrina	Concordia University	maria@cermm.concordia.ca
Farnaz Shakib	University of Alberta	shakib@ualberta.ca
Bharat Kumar Sharma	Concordia University	bharatsharma61@hotmail.com
Lena Simine	University of Toronto	etstrubal@gmail.com
Viktor Staroverov	University of Western Ontario	vstarove@uwo.ca
Pawel Tecmer	McMaster University/P.W.Ayers	ptecmer@gmail.com
Mark Thachuk	University of British Columbia	thachuk@chem.ubc.ca
Ajit Thakkar	University of New Brunswick	ajit@unb.ca
Philippe Thomas	Queen's University	p.s.thomas@umail.leidenuniv.nl
Qadir Timerghazin	Marquette University	qadir.timerghazin@mu.edu
Anna Tomberg	McGill University	anna.tomberg@mail.mcgill.ca
Eric Toombs	Queen's University	e.toombs@queensu.ca
Amin Torabi	University of Western Ontario	mtorabi@uwo.ca

Troy VanVoorhis	Massachusetts Institute of Technology	tvan@mit.edu
Jérémy Viau-Trudel	Université Laval	jeremy.viau-trudel.1@ulaval.ca
Xiaogang Wang	Queen's University	xgwang.dalian@gmail.com
Lecheng Wang	University of Waterloo	lecheng@sciborg.uwaterloo.ca
rodrigo wang	Université de Montréal	rodrigobogossian@gmail.com
Xijun Wang	Concordia University	xijunw@gmail.com
Alex Wang	University of British Columbia	yawang@chem.ubc.ca
Haobin Wang	New Mexico State University	haobin@nmsu.edu
Dongqing Wei	Shanghai Jiaotong University	dqwei@sjtu.edu.cn
Tony Whitehead	McGill University	tony.whitehead@mcgill.ca
Sarah Whittleton	University of California Merced	swhittleton@ucmerced.edu
Weitao Yang	Duke University	weitao.yang@duke.edu
Spencer Yim	University of Waterloo	sbyim@uwaterloo.ca
Mohammad Zein Aghaji	University of Ottawa	mohammadzeinaghaji@gmail.com
Dongbin Zhang	University of Waterloo	ecpgieicg@gmail.com
Yongxi Zhou	Université de Montréal	quangeez@gmail.com
Tom Ziegler	University of Calgary	ziegler@ucalgary.ca