

CSTC2010

**17th Canadian Symposium on Theoretical Chemistry
Le 17ième Symposium Canadien de Chimie Théorique**

Book of Abstracts & Program

**Lister Conference Centre
University of Alberta
Edmonton, Alberta, Canada
July 25-30, 2010**

www.cstc2010.ca



Welcome to the 17th Canadian Symposium on Theoretical Chemistry
Bienvenue au 17e symposium canadien de chimie théorique

Welcome to Edmonton and to the University of Alberta

Held every three years, the Canadian Symposium on Theoretical Chemistry is an international meeting bringing together theoretical chemists from across Canada and around the world. The symposium is intended to cover the full scope of theoretical chemistry, including electronic structure methods, chemical dynamics, and statistical mechanics, with a particular focus on recent theoretical and methodological advances. The 2010 meeting is the 17th in a series dating back to the inaugural Symposium held here, at the University of Alberta in 1965. The 1965 Symposium was the first in Canada dedicated exclusively to theoretical chemistry.

We are pleased to acknowledge the financial assistance of the:

Department of Chemistry of the University of Alberta

Department of Chemistry of the University of British Columbia

Physical, Theoretical, and Computational division of the Canadian Society for Chemistry

Canadian Association of Theoretical Chemists

We would like to offer our sincere gratitude to Jill Bagwe and Traci Grams of the Department of Chemistry and Kevin Moodie from AICT at the University of Alberta who have been helpful above and beyond the “call of duty”, as well as to the graduate students in the theory groups at the University of Alberta (Marie Barnes, Bryan Faucher, Amelia Fitzsimmons, Melissa Gajewski, Stephanie Wong, Wang Xi, Ryan Zaari, Toby Zeng) for volunteering their time and effort.

We hope you will enjoy your visit and the program of the 17th Canadian Symposium on Theoretical Chemistry.

Sincerely,

Alex Brown
Department of Chemistry
University of Alberta
Edmonton, AB
Canada

Mariusz Klobukowski
Department of Chemistry
University of Alberta
Edmonton, AB
Canada

Pierre-Nicholas Roy
Department of Chemistry
University of Waterloo
Waterloo, ON
Canada

Mark Thachuk
Department of Chemistry
University of British Columbia
Vancouver, BC
Canada

Beginning this year, a new element has been added to the format of the Symposium - the Canadian Association of Theoretical Chemists (CATC) Honorary Lecture. This Honorary Lecture establishes a new tradition of recognizing the contributions of an individual to the Canadian theoretical chemistry community. The Organizing Committee has decided that our colleague Russell Boyd from the Department of Chemistry at Dalhousie University will deliver the inaugural CATC Honorary Lecture "Theoretical Chemistry in Canada: A Personal Perspective" (on Thursday at 4:40pm). A brief biography of Russell Boyd appears below.

Russell Boyd is the Associate Vice-President (Research) and Alexander McLeod Professor of Chemistry. He joined Dalhousie University in 1975 and rose through the ranks to become a Professor in 1985. He served as the Chair of Chemistry from 1992 to 2005. He was a Killam Professor from 1997 to 2002 and in 2001 was named the Alexander McLeod Professor of Chemistry.

He is a Fellow of the Chemical Institute of Canada and has served the Canadian Society for Chemistry in many capacities, including as President, 2007 to 2008. He was awarded the Montreal Medal of the Chemical Institute of Canada in 2009 in recognition of his contributions to chemistry in Canada. He is the only elected Canadian member of the Board of the World Association of Theoretical and Computational Chemists.

His research interests span a range of topics in computational and theoretical chemistry with an emphasis on problems relevant to biological systems. He has published about 240 research papers and twelve review chapters. He co-edited "The Quantum Theory of Atoms in Molecules" with Chérif Matta in 2007. He has supervised the research of 20 PhD students, more than 25 postdoctoral fellows and senior visitors, and a comparable number of undergraduate students. Fourteen former members of his group hold academic appointments at Canadian universities and another eight hold similar appointments abroad.

Information

Program

All oral presentations will take place in the Maple Leaf Room on the second floor of the Lister Conference Centre. A listing of abstracts begins on page 9. The abstracts for oral presentations are listed first in the order of presentation and are prefixed with “O” while those for poster presentations are divided approximately alphabetically into “A” and “B” groups. An author index of all abstracts can be found at the end of the book.

Poster sessions will be held on Tuesday and Thursday afternoons in the Aurora and Prairie Rooms on the second floor of the Lister Conference Centre. Posters for the Tuesday afternoon “A” session should be put up on Monday morning but should be removed by Wednesday morning. Posters for the Thursday afternoon “B” session should be put up on Wednesday afternoon but should be removed by Friday morning.

The business meeting of the Canadian Association of Theoretical Chemists will be held on Wednesday at 4:40pm in the Maple Leaf Room. All Canadian faculty are encouraged to attend. A number of important motions will be presented for discussion and voting so it is important to have good attendance.

The Opening Reception for the Symposium will be held on Sunday evening beginning at 6:30pm in the Wild Rose Room on the second floor of the Lister Conference Centre. All coffee breaks and lunches will also be served in the Lister Conference Centre. However, the Symposium Banquet will be held at a different location on campus, at Alumni House. Please consult the campus map on page 8 for the location of Alumni House (which appears in the top left hand corner of the map).

A table showing the program in a compact form can be found on page 4.

Light Rail Transit (LRT) and Bus Service

For those staying at hotels downtown, the quickest and easiest way to the Lister Conference Center is by LRT. The nearest LRT stop to the conference centre is Health Sciences/Jubilee. You can also stop at University. A map of the LRT is included on page 5. During peak hours (Monday to Friday 6:00am-9:00am and 2:00pm-6:00pm) the train runs every 5 minutes. From 9:00am-2:00pm (Monday to Friday) and from 6:00am-6:00pm (Saturday and Sunday) the train runs every 10 minutes. After 6:00 pm it runs every 15 minutes.

Many restaurants and bars are located on Whyte (82nd) Avenue and a table listing some of these can be found on page 3. Whyte Avenue is an approximately 20-25 minute walk from the conference centre. Several buses, which depart from the University LRT/Bus Terminal, will also take you along Whyte Avenue. Routes 4 (Capilano), 7 (Jasper Place), 57 (Downtown), and 106 (Capilano) all travel down Whyte Avenue and depart on a regular basis during the day and early evening.

Since some of you may want to take time to visit the West Edmonton Mall (www.wem.ca), a bus route map for Route #4 travelling from the University LRT/Bus Terminal to the Mall and back has been enclosed on page 6. The bus departs every 15 minutes from 6:00am-10:00pm and the bus ride is approximately 35 minutes long.

Fares on the bus and LRT are \$2.75/adult (bus is exact change only, no bills) or you may purchase a book of 10 tickets for \$22.00. Books of bus tickets are available from most convenience stores. When travelling on the LRT retain your time-stamped ticket as it may be used on either the LRT or bus for 90-minutes after first being validated. When travelling on the bus, be sure to ask for a transfer upon entry, as this transfer can be used on subsequent bus or LRT travel for 90 minutes after first boarding.

Further information on the bus and LRT routes and schedules is available at www.takeets.com

Selected Restaurants Near Campus and on Whyte (82) Avenue Accessible by Walking or Bus

Entree Prices: \$ - \$10, \$\$- \$20, \$\$\$ - \$30 [* to ***** Rating] V: Vegetarian Recommended

Sugar Bowl Coffee & Juice Bar 10922 88 Avenue Northwest (780) 433-8369 thesugarbowl.org Pub/Bar, assorted food, \$-\$\$, ***, V	Boston Pizza 10854 82 Avenue Northwest (780) 450-2900 bostonpizza.com Sports bar/restaurant, \$-\$\$, **1/2	Twisted Fork Diner 11612 82 Avenue Northwest (780) 761-3675 twisted-fork.ca Casual Dining, \$-\$\$, **1/2
Chianti Cafe & Restaurant 10501 82 Avenue Northwest (780) 439-9829 chianticafe.ca Pasta (fresh), \$\$, ***	Dadeo 10548 82 Avenue Northwest (780) 433-0930 dadeo.ca Cajun Diner, \$-\$\$,***1/2 V	Oodle Noodle Box 10803 82 Avenue Northwest (780) 988-7808 oodlenoodle.ca Noodle Boxes, \$, **
Original Joe's 18404 109 Street Northwest (780) 988-5800 originaljoes.ca Pub/Bar, Pub Food, \$-\$\$, **1/2	Remedy Cafe 8631 109 Street Northwest (780) 433-3096 remedycafe.ca Beer, Curry and Cake, \$, **, V	Avenue Pizza 8519 112 Street Northwest (780) 432-0536 Sports bar/restaurant, \$-\$\$, **1/2
HighLevel Diner 10912 88 Avenue Northwest (780) 433-0993 highleveldiner.com Assorted food, \$-\$\$, ***, V	Kyoto Japanese Cuisine Ltd 8701 109 Street Northwest (780) 414-6055 Sushi, \$\$\$, ****	Keg Steakhouse & Bar 8020 105 Street Northwest (780) 432-7494 kegsteakhouse.com Steaks, \$\$\$, ***1/2
Furusato Japanese Restaurant 10012 82 Avenue Northwest (780) 439-1335 Sushi, \$\$\$, ****	Vons Steak House & Oyster Bar 10309 81 Avenue Northwest (780) 439-0041 vonssteakhouse.com Steaks, \$\$\$, ****	Hudsons On Campus 11113 87 Avenue Northwest (780) 433-6364 hudsonstaphouse.com Pub food, \$-\$\$, **1/2
Earls Restaurant 8629 112 Street Northwest (780) 439-4848 earls.ca Western cuisine, \$\$, ***	Chili's Texas Grill 8217 104 Street Northwest (780) 431-2662 Assorted Tex Mex Food, \$\$, **	Langano Skies Ethiopian Restaurant 9920 82 Avenue Northwest (780) 432-3334 langanoskies.com Ethiopian Food, \$\$, ****
Doan's Restaurant 7909 104 Street Northwest (780) 424-3034 doans.ca Vietnamese, \$-\$\$, ***	Packrat Louie Kitchen and Bar 10335 83 Avenue Northwest (780) 433-0123 packratlouie.com Fine Dining, Good wine, \$\$\$, ****	Murrieta's Bar and Grill 10612 82 Avenue Northwest (780) 438-4100 murrietas.ca Fine Dining, Good wine, \$\$\$, ****
Cafe Mosaics 10844 82 Avenue Northwest (780) 433-9702 Vegetarian, \$\$, ***	Julio's Barrio Mexican Restaurant 10450 82 Avenue Northwest (780) 431-0774 juliosbarrio.com Mexican, Margaritas, \$\$, *	O'Byrnes Irish Pub 10616 82 Avenue (780) 414-6766 obyrnes.com Pub/Bar, Pub Food, \$-\$\$, **1/2

Selected Restaurants Downtown: Accessible by LRT

Entree Prices: \$ - \$10, \$\$- \$20, \$\$\$ - \$30 [* to ***** Rating] V: Vegetarian Recommended

Khazana Restaurant 10177 107 Street Northwest (780) 702-0330 khazana.ab.ca Indian (Buffet Wed. Night), \$\$, ***	The Mongolie Grill 10104 109 Street Northwest (780) 420-0037 themongoliegrill.com Make your own Stir Fry, \$\$, ***, V	Hardware Grill 9698 Jasper Avenue Northwest (780) 423-0969 hardwaregrill.com Fine Dining, Good wine, \$\$\$, ****
Sicilian Pasta Kitchen 11239 Jasper Avenue Northwest (780) 488-3838 Pasta, \$\$, ***1/2	Bua Thai Restaurant 10049 113 Street Northwest (780) 482-2277 Thai, \$\$, ****, V	Ric's Grill Downtown Edmonton 10190 104 Street Northwest (780) 429-4333 ricsgrilledmonton.com Western, \$\$\$, ***
The Creperie 10220 103 Street Northwest (780) 420-6656 thecreperie.com French, \$\$\$, ****	Haweli Restaurant 10220 103 Street Northwest (780) 421-8100 haweli.ca Indian, \$\$, ***1/2, V	Padmanadi Vegetarian 10626 97 Street Northwest (780) 428-8899 padmanadi.com Vegetarian, \$\$, ****1/2, V

Time	Sunday July 25	Monday July 26	Tuesday July 27	Wednesday July 28	Thursday July 29	Friday July 30
8:45-9:00		Jonathan Schaeffer Vice-Provost and AVP (Information Technology) Chair: Ajit Thakkar	Chair: Peter Kusalik	Chair: Tucker Carrington Jr.	Chair: John Goddard	Chair: Qadir Timerghazin
9:00-9:40		How Do Electrons Fragment Peptides in Electron Transfer Dissociation (ETD) Mass Spectrometry? Jack Simons (O1)	Theory of Monovalent Cation Selectivity in Protein Binding Sites Sergei Noskov (O9)	Quantum Biology of Photosynthesists in Purple Bacteria Klaus Schulten (O16)	Improving Reptation Quantum Monte Carlo Stuart Rothstein (O24)	The Role of Solvent Polarization in the Spectroscopy of the Hydrated Electron John Hebert (O31)
9:40-10:20		Modeling Enzyme-Catalyzed Reactions Using Semitemperical Methods James Stewart (O2)	From Water Structure and Fluctuations to Hydrophobicity of Proteins and Interfaces Shekhar Garde (O10)	Reaction Kinetics in Viscous Media: Molecular Dynamics and Stochastic Models Noham Weinberg (O17)	DFT - Koopmans' Theorem Kimihiko Hirao (O25)	Time-Dependent Density Functional Theory for Open Quantum Systems and Its Linear-Response Implementation Alán Aspuru-Guzik (O32)
10:20-11:00		Coffee Break Chair: Marcel Nooijen	Coffee Break Chair: Gilles Peslherbe	Coffee Break Chair: Alex Wang	Coffee Break Chair: Tom Ziegler	Coffee Break Chair: René Fournier
11:00-11:40		Local Correlation Coupled-Cluster Methods Exploiting Cluster-in-Molecule Ansatz and their Multi-Level Generalizations Piotr Piecuch (O3)	Computer Simulations of Lipids Peter Tieleman (O11)	Correlated Dynamics of the Double Hydrogen Bonds of Adenin-Uracil Base Pairs in Solution Oliver Kühn (O18)	First-Principles Simulations of Tribological Processes Nicholas Mosey (O26)	Toward Accurately Predictive Quantum Chemistry with the Solutions of the Schrödinger and Dirac-Coulomb Equations Hiroshi Nakatsuji (O33)
11:40-12:20	4	Advances in Multireference Coupled Cluster Theory Wesley Allen (O4)	Hybrid Potential Simulations of Enzyme Catalysis Martin Field (O12)	Quantum Molecular Dynamics Studies with MCTDH: Applications to H ₅ O ₂ ⁺ and Malonaldehyde Hans-Dieter Meyer (O19)	Advances in the Simulation of Nanoporous Materials for Carbon Dioxide Capture Tom Woo (O27)	The Accuracy of the Pseudopotential Approximation Peter Schwerdtfeger (O34)
12:20-13:00		Explicitly Correlated CASPT2 and MRCI Methods Hans-Joachim Werner (O5)	Theoretical Studies of Enzymes Walter Thiel (O13)	Quantum Transport and Quantum Information in Molecules Koichi Yamashita (O20)	Interacting Electrons Confined in Cavities of Almost Arbitrary Shape Viktor Staroverov (O28)	Heavy Elements' Chemistry with Relativistic Model Core Potential and Recent Large-scale Molecular Theory Hirotoshi Mori (O35)
13:00-14:40		Lunch Chair: Gino Di Labio	Lunch and Poster Session A	Lunch Chair: Matthias Ernzerhof	Lunch and Poster Session B	End Of Symposium
14:40-15:20		Theory and Modeling for Energy Applications: Charge Transport in Complex Molecular and Solid State Environments Michel Dupuis (O6)		Adaptive Multiscale Molecular Dynamics Simulations of Soft Matter Steve Nielsen (O21)		
15:20-16:00		Self-assembly at the Solid Surface: Theoretical Models and Mechanisms Irina Paci (O7)		Coherent Control of the Photoassociation of Ultracold Molecules Christiane Koch (O22)		
16:00-16:40		Theories of Metal Nanoparticle Optical Properties: Bottom-up Meets Top-down George Schatz (O8)	Chair: Regis Pomes	Tunable Excitations in Ordered Arrays of Ultracold Molecules on Optical Lattices Roman Krems (O23)	Chair: Dennis Salahub	
16:40-17:20			Semiempirical Quantum Models for Metalloenzymes Guillaume Lamoureux (O14)	Canadian Association of Theoretical Chemists (CATC) Business Meeting	Correlation from the Electron Pair Perspective Jason Pearson (O29)	CATC Honorary Lecture Theoretical Chemistry in Canada: A Personal Perspective Russell Boyd (O30)
18:30	Opening Reception		The Signature of Nonadiabatic Transitions on the Pump-Probe Infrared Spectra of a Hydrogen-bonded Complex Dissolved in a Polar Solvent Gabriel Hanna (O15)			Symposium Banquet

ROUTE LRT

Map revised April 25, 2010

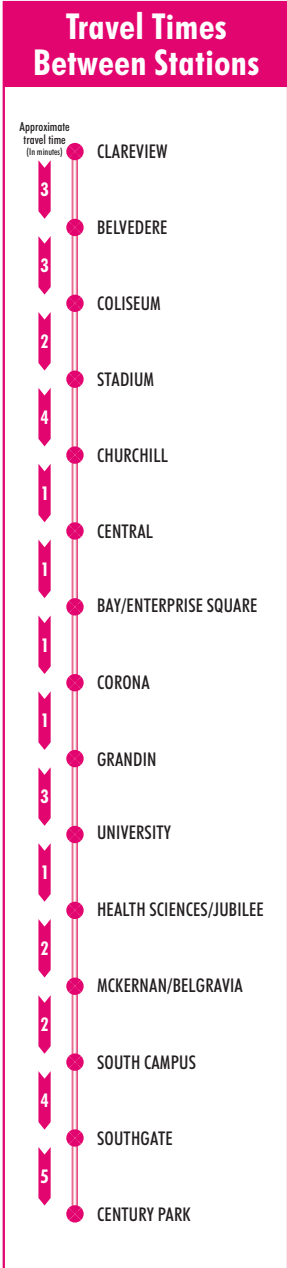
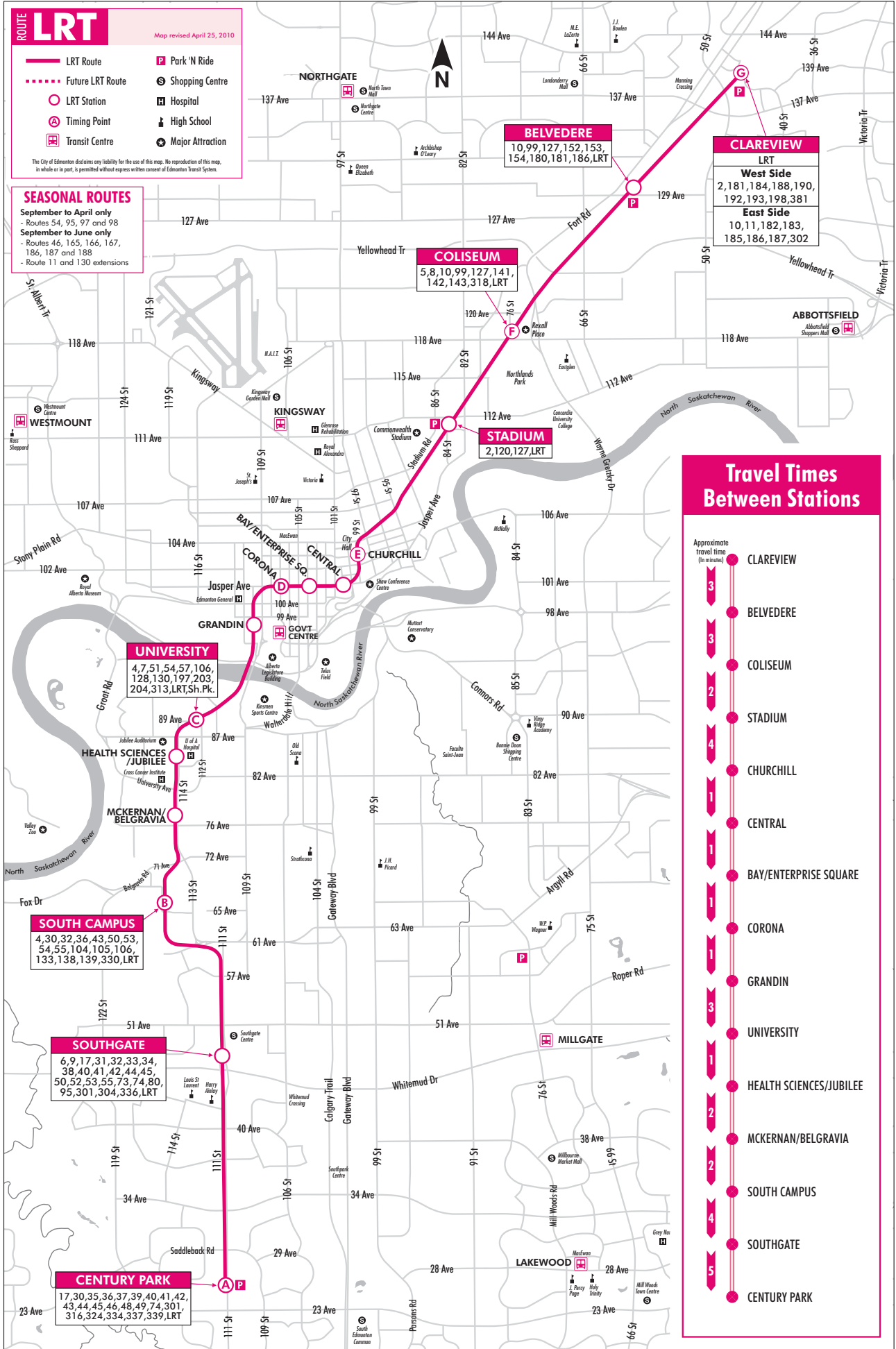
- LRT Route
- ⋯ Future LRT Route
- LRT Station
- ⌚ Timing Point
- ⊠ Transit Centre
- Ⓟ Park 'N Ride
- 🛒 Shopping Centre
- 🏥 Hospital
- 🎓 High School
- 🎪 Major Attraction

The City of Edmonton disclaims any liability for the use of this map. No reproduction of this map, in whole or in part, is permitted without express written consent of Edmonton Transit System.

SEASONAL ROUTES

September to April only
- Routes 54, 95, 97 and 98

September to June only
- Routes 46, 165, 166, 167, 186, 187 and 188
- Route 11 and 130 extensions



BELVEDERE
10, 99, 127, 152, 153, 154, 180, 181, 186, LRT

CLAREVIEW
LRT
West Side
2, 181, 184, 188, 190, 192, 193, 198, 381
East Side
10, 11, 182, 183, 185, 186, 187, 302

COLISEUM
5, 8, 10, 99, 127, 141, 142, 143, 318, LRT

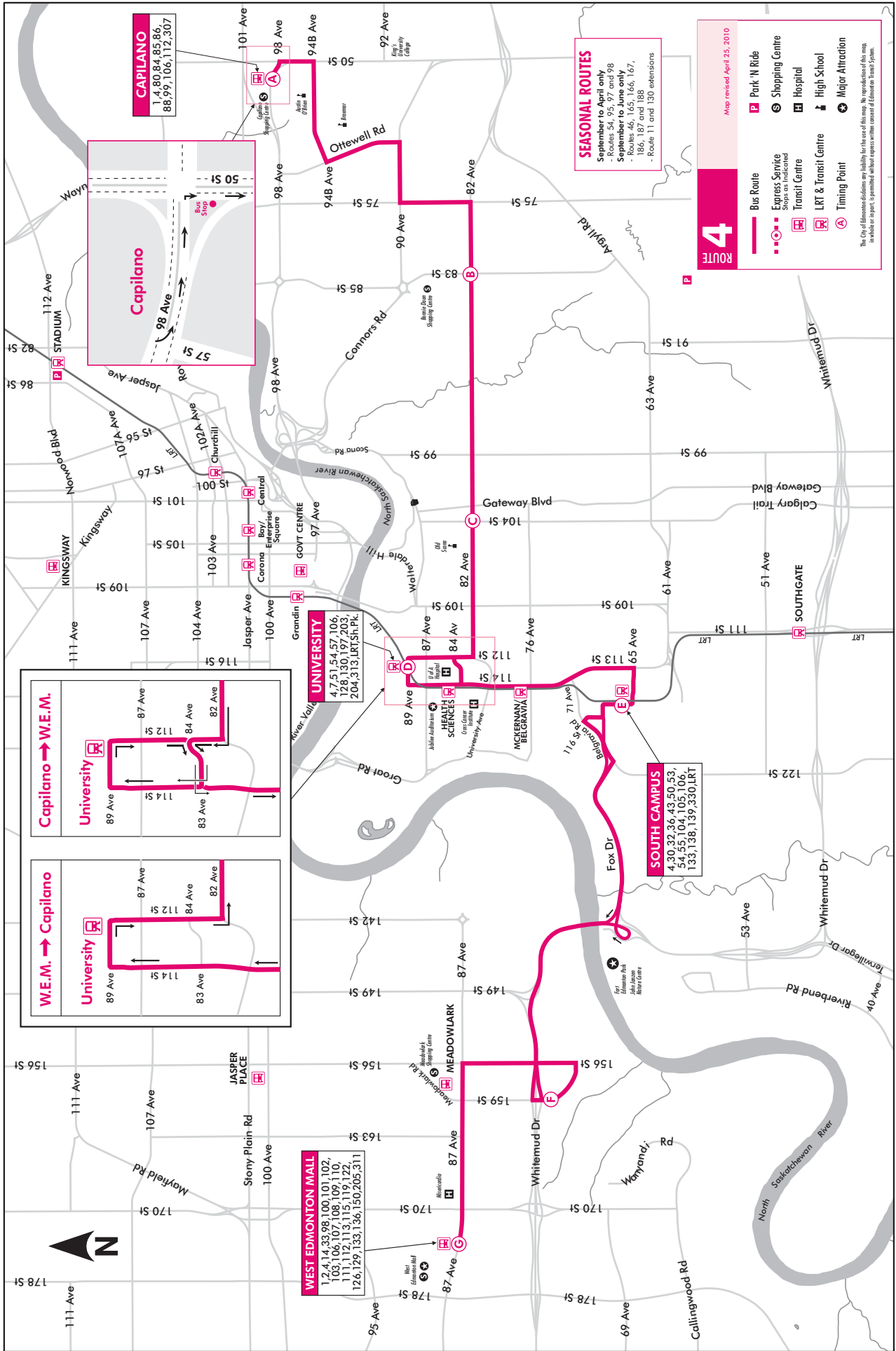
STADIUM
2, 120, 127, LRT

UNIVERSITY
4, 7, 51, 54, 57, 106, 128, 130, 197, 203, 204, 313, LRT, Sh. Pk.

SOUTH CAMPUS
4, 30, 32, 36, 43, 50, 53, 54, 55, 104, 105, 106, 133, 138, 139, 330, LRT

SOUTHGATE
6, 9, 17, 31, 32, 33, 34, 38, 40, 41, 42, 44, 45, 50, 52, 53, 55, 73, 74, 80, 95, 301, 304, 336, LRT

CENTURY PARK
17, 30, 35, 36, 37, 39, 40, 41, 42, 43, 44, 45, 46, 48, 49, 74, 301, 316, 324, 334, 337, 339, LRT



CAPILANO
 7,4,80,84,85,86,
 88,99,106,112,307

Capilano → W.E.M.

University

W.E.M. → Capilano

University

WEST EDMONTON MALL
 1,2,4,14,33,98,100,101,102,
 103,106,107,108,109,110,
 111,112,113,115,119,122,
 126,129,133,136,150,205,311

UNIVERSITY
 4,7,51,54,57,106,
 128,130,197,203,
 204,313,LRT,Sh.Pk.

SOUTH CAMPUS
 4,30,32,36,43,50,53,
 54,57,101,102,118,
 133,138,139,230,LRT

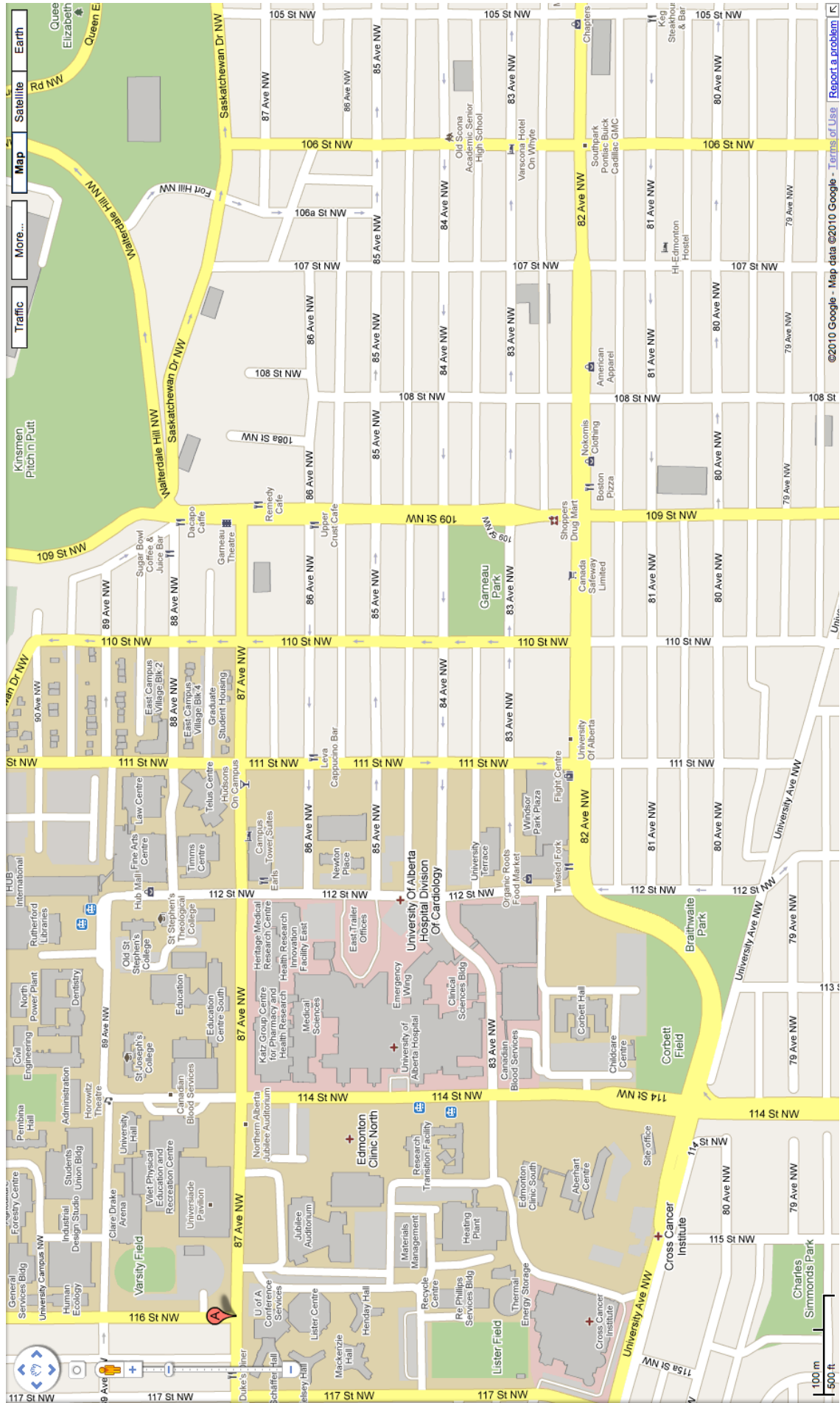
SEASONAL ROUTES
 September to April only
 - Routes 54, 95, 97 and 98
 September to June only
 - Routes 46, 165, 166, 167,
 186, 187 and 188
 - Route 11 and 130 extensions

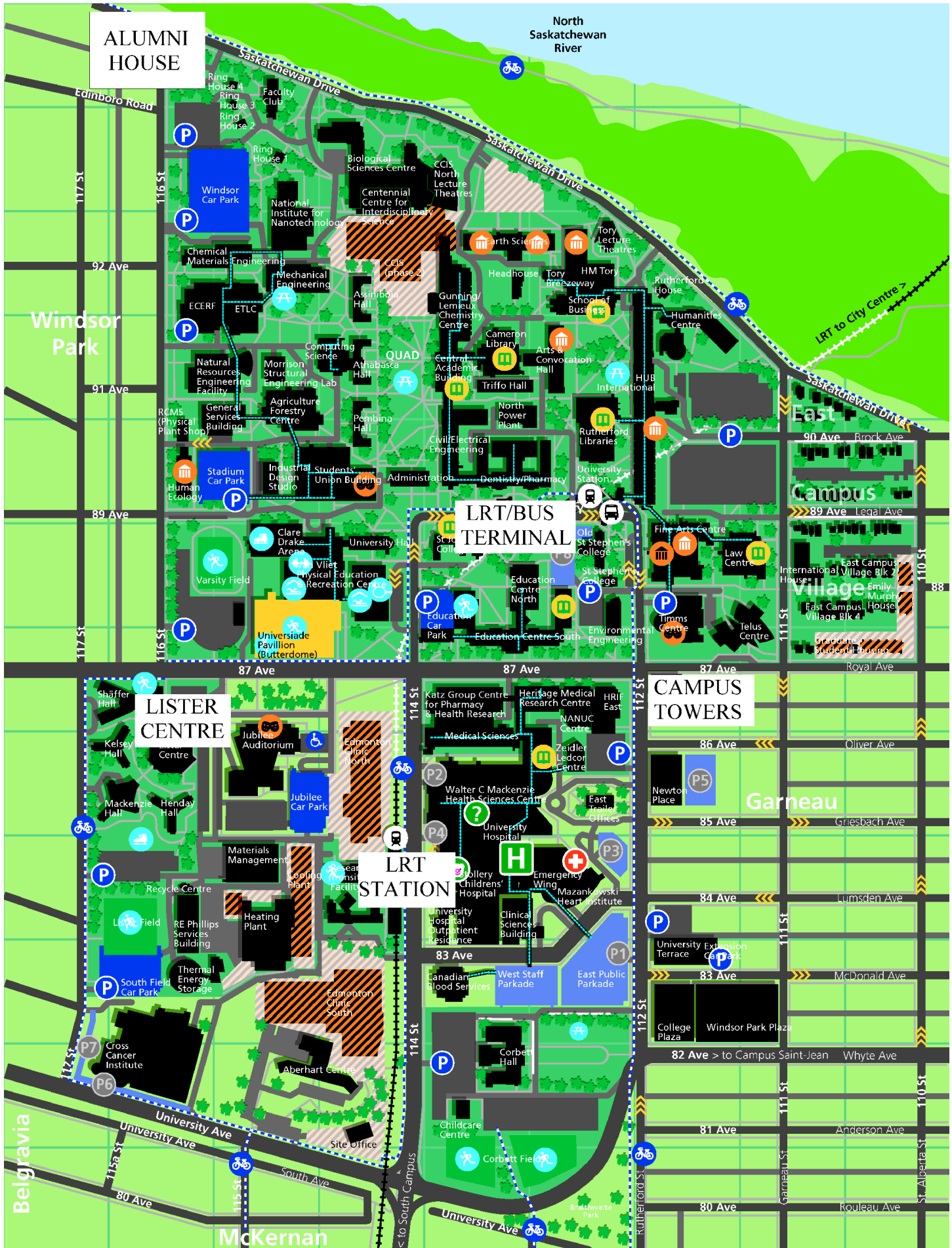
ROUTE 4

Map revised April 25, 2010

- Bus Route
- Express Service Stops as Indicated
- Transit Centre
- LRT & Transit Centre
- Timing Point
- Park 'N Ride
- Shopping Centre
- Hospital
- High School
- Major Attraction

The City of Edmonton disclaims any liability for the use of this map. No reproduction of this map in whole or in part is permitted without express written consent of Edmonton Transit System.





Abstracts

O1

How Do Electrons Fragment Peptides in Electron Transfer Dissociation (ETD) Mass Spectrometry?

Jack Simons

Department of Chemistry, University of Utah, 315 S. 1400 E., Salt Lake City, Utah 84112
USA

In electron-transfer mass spectrometry (ETD), an electron attaches to a multiply positively charged gas-phase polypeptide and breaks one of its bonds. It is observed that SS and N – C α bonds are most often cleaved. We have been involved in trying to determine (i) where in the polypeptide does the electron initially attach? (ii) whether the electron stay there or migrates and, if so, how? (iii) why the SS and N – C α bonds break even though peptide bonds are weaker than N – C α bonds. This work involves inter- and intra-molecular electron transfers, Rydberg orbitals, excited states, and other fun subjects.

Modeling Enzyme-Catalyzed Reactions Using Semiempirical Methods*James Stewart*

Stewart Computational Chemistry

Using the newly-developed semiempirical method PM6, the linear scaling SCF procedure MOZYME, and the low-memory function minimizer L-BFGS, various features of enzyme catalyzed reactions were investigated. Mechanisms examined range from simple reactions, such as the Claisen chorismate-prehenate isomerization and the Kemp elimination in the ring-opening of 5-nitrobenzoxazole, to more complicated systems, specifically the carboxylate and imidazole-carboxylate dyad base catalyzed hydrolysis of peptide bonds. Some of the issues and features found in these systems will be discussed, such as the computational effort required, the nature of the environment of the substrate in chymotrypsin hydrolysis, and the mechanism used in aspartate protease.

Local Correlation Coupled-Cluster Methods Exploiting Cluster-in-Molecule Ansatz and their Multi-Level Generalizations

Piotr Piecuch and Wei Li

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, USA

Coupled-cluster (CC) methods have greatly impacted modern quantum chemistry, but, as all electronic structure approaches that aim at the accurate description of many-electron correlation effects, they face significant challenges when dealing with the increasingly complex molecular problems chemists are interested in. This includes prohibitive costs of CC calculations for larger molecular systems. To help to address this challenge, we have extended [1,2] a number of CC methods, including CCSD, CCSD(T), and the completely renormalized extension of CCSD(T), abbreviated as CR-CC(2,3) [3], to larger systems with hundreds of atoms through the use of the local correlation, cluster-in-molecule (CIM) ansatz [1,2,4]. The resulting CIM-CCSD, CIM-CCSD(T), and CIM-CR-CC(2,3) methods are characterized by (i) the linear scaling of the CPU time with the system size when the same level of theory is applied to all CIM subsystems, (ii) the use of orthonormal orbitals in subsystem calculations, (iii) the natural coarse-grain parallelism, which can be further enhanced by the additional fine-grain parallelism of each subsystem calculation, (iv) the high computational efficiency, enabling calculations for large molecular systems at high levels of CC theory, (v) the purely non-iterative character of local triples corrections to CCSD energies, and (vi) the applicability to the covalently and weakly bound molecular systems. In addition, one can use the flexibility of the CIM local correlation ansatz to mix different CC or CC and non-CC methods within a single calculation, enabling the rigorous formulation of multi-level local correlation theories [2] that combine the high-level CC methods, such as CR-CC(2,3), to treat, for example, the reactive part of a large molecular system with the lower-order *ab initio* (e.g., MP2) scheme(s) to handle the chemically inactive regions without splitting it into *ad hoc* fragments and saturating dangling bonds. By comparing the results of the canonical CC calculations with the single- and multi-level CIM-CC calculations for normal alkanes [1,2], water clusters [1], the diffusion of atomic oxygen on the silicon surface [5], and the proton transfer in the aggregates of dithiophosphinic acids with water [2], we demonstrate that the CIM-CCSD, CIM-CCSD(T), and CIM-CR-CC(2,3) approaches, and their multi-level extensions accurately reproduce the corresponding canonical CC correlation and relative energies, including chemical reaction pathways, while offering savings in the computer effort by orders of magnitude.

References

- [1] (a) W. Li, P. Piecuch, J. R. Gour, and S. Li, *J. Chem. Phys.* **131**, 114109 (2009). (b) W. Li, P. Piecuch, and J. R. Gour, in: *Theory and Applications of Computational Chemistry - 2008*, AIP Conference Proceedings, Vol. 1102, edited by D.-Q. Wei and X.-J. Wang (AIP, Melville, NY, 2009), p. 68. (c) W. Li, P. Piecuch, and J. R. Gour, in: *Progress in Theoretical Chemistry and Physics*, Vol. 19, *Advances in the Theory of Atomic and Molecular Systems: Conceptual and Computational Advances in Quantum Chemistry*, edited by P. Piecuch, J. Maruani, G. Delgado-Barrio, and S. Wilson (Springer, Dordrecht, 2009), p. 131. (d) W. Li and P. Piecuch, *J. Phys. Chem. A*, in press; Articles ASAP; Publication Date (Web): April 7, 2010.
- [2] W. Li and P. Piecuch, *J. Phys. Chem. A*, in press.
- [3] (a) P. Piecuch and M. Wloch, *J. Chem. Phys.* **123**, 224105 (2005). (b) P. Piecuch, M. Wloch, J. R. Gour, and A. Kinal, *Chem. Phys. Lett.* **418**, 467 (2006).
- [4] (a) S. Li, J. Ma, and Y. Jiang, *J. Comput. Chem.* **23**, 237 (2002). (b) S. Li, J. Shen, W. Li, and Y. Jiang, *J. Chem. Phys.* **125**, 074109 (2006).
- [5] P. Arora, W. Li, P. Piecuch, J. W. Evans, M. Albao, and M. S. Gordon, *J. Phys. Chem. C*, submitted.

Advances in Multireference Coupled Cluster TheoryWesley AllenCenter for Computational Chemistry and Department of Chemistry, University of Georgia,
Athens, Georgia 30602 USA

A state-specific and rigorously size-extensive multireference coupled cluster theory (Mk-MRCC) and a companion second-order perturbation theory (Mk-MRPT2) have been developed into powerful and practical tools for chemical research. The effectiveness of our Mk-MRCC methods is established by extensive computations on benchmark problems, including the low-lying electronic states of O₂, CH₂, and H₂CO, the dissociation of F₂, and the ozone graveyard for theory. In chemical applications of Mk-MRCC theory, outstanding results have been obtained for the optimum geometric structures, vibrational frequencies, and electronic excitation energies of the organic diradicals *ortho*-, *meta*-, and *para*-benzyne, as well as the cyclic polyenes cyclobutadiene and cyclooctatetraene. A rigorous Mk-MRCC torsional surface has been generated for the classic problem of the stereomutation of cyclopropane. The seemingly simple organic molecule cyclobutanetetraone (C₄O₄) is demonstrated by Mk-MRCC theory to actually have a triplet rather than a closed-shell singlet ground state! Finally, joint theoretical and experimental work is presented on novel hydroxycarbenes (RCOH; R = H, CH₃, and phenyl) that has led to the first isolation and identification of these species. These hydroxycarbenes show rapid tunneling ($t_{1/2} \approx 2$ hrs) at 11 K through prodigious energy barriers of 30 kcal mol⁻¹, a remarkable phenomenon confirmed by our high-accuracy computations of barrier penetration integrals. In the case of methylhydroxycarbene, a surprising mechanism is witnessed - *tunneling control* that yields a different product than that expected from traditional kinetic control of the chemical reaction.

Explicitly Correlated CASPT2 and MRCI Methods*Hans-Joachim Werner, Gerald Knizia, K.R. Shamasundar and Toru Shiozaki*Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, D-70569
Stuttgart

A new CASPT2-F12 method [1] is presented, which includes explicitly correlated terms in the first-order wave function. This dramatically improves the basis set convergence at little extra cost. The intermediates are very similar as in closed-shell MP2-F12 theory, and the required density matrices and coupling coefficients are the same as in standard CASPT2. In addition, a new internally contracted multi-reference configuration interaction (IC-MRCI) method [2] is presented. In contrast to the existing IC-MRCI method [3], not only the doubly external configurations but also most of the semi-internal and internal configuration classes are internally contracted, as proposed earlier for CASPT2 [4]. All required coupling coefficients and density matrices involve only indices of the active orbitals of the reference function, making it possible to correlate much larger inactive spaces than previously. The required working equations are highly complex and could only be derived and implemented automatically. In our approach, the entire equation network is transformed into an optimized sequence of binary tensor contractions. These are then evaluated with a new Virtual Tensor Network (VTF) [5]. The tensors represent wave function parameters, integrals, density matrices, or other intermediates. The network evaluation algorithm is executed on a virtual machine, which contains the computational kernel and efficiently handles spatial and permutational symmetries as well as other implementation details. For cases with many inactive orbitals, the new IC-MRCI method is an order of magnitude faster than the previous one. The VTF has also been used to implement other methods, e.g. MP2-F12 and CCSD(T), and the efficiency of the hand-coded programs in MOLPRO is matched or even exceeded.

References

- [1] T. Shiozaki and H.-J. Werner, submitted for publication.
- [2] K. R. Samasundar, G. Knizia, and H.-J. Werner, to be published.
- [3] H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **89**, 5803 (1988).
- [4] P. Celani, H.-J. Werner, *J. Chem. Phys.* **112**, 5546 (2000).
- [5] G. Knizia and H.-J. Werner, to be published.

Theory and Modeling for Energy Applications: Charge Transport in Complex Molecular and Solid State Environments

Michel Dupuis

Chemical and Materials Sciences Division, Pacific Northwest National Laboratory,
Richland WA, USA

In this presentation we will highlight investigations of charge transport and reactivity in complex environments relevant to energy applications: (1) e-/h+ polaron structure, transport, trapping in TiO₂ and their relevance to the reactivity of oxygenated species on TiO₂, all issues relevant to light-to-chemical energy conversions; proton transport in polymeric electrolyte membrane (PEM) relevant to chemical energy-to-electricity conversion; multi-electron and proton reactions in electrocatalysis for electricity to fuel inter-conversion. This work makes use of modern computational methodologies in DFT and *ab initio* molecular dynamics MD.

Self-assembly at the Solid Surface: Theoretical Models and Mechanisms*Irina Paci, Chris Chapman and Tatiana Popa*

Department of Chemistry, University of Victoria, PO Box 3065, Victoria, BC, V8W 3V6

The cutting edge of nanotechnology research is the bottom-up creation of devices with complex functions. In this context, miniaturization of devices towards the single-molecule scale can be efficiently achieved by designing components to self-assemble and realize the desired structure or complex. Theoretical investigations of surface self-assembly are challenging because quantum mechanical information about the molecules, the surface, and their interactions must ultimately be incorporated in bulk simulations. This talk will describe some of our group's efforts to advance the 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 detail. An on-going project, focused on the switching behavior of mixed diazobenzene/alkylthiol monolayers on gold, will also be presented.

**Theories of Metal Nanoparticle Optical Properties: Bottom-Up Meets
Top-Down***George Schatz*

Department of Chemistry, Northwestern University, Evanston IL 60208-3113 USA

This talk will describe our recent efforts to improve on classical electromagnetic theory in the description of metal nanoparticle (plasmonic) optical properties, with emphasis on surface enhanced Raman spectroscopy. A top-down approach involves the use of nonlocal dielectric response in classical electrodynamics. We have recently developed a method for embedding this into the finite-difference time-domain (FDTD) method, and this allows us to study both small particles and small gaps between big particles at a higher level than in past work, including for single-electron excitations as well as plasmon excitations. The bottom-up theory that we use is real time TDDFT. Here I will describe a series of projects that we have done that enables us to describe the optical properties of metal clusters with up to 1000 atoms, providing an important glimpse as to the connection between electronic structure and electrodynamics. I will also discuss the development of hybrid methods that couple TDDFT to FDTD.

Theory of Monovalent Cation Selectivity in Protein Binding Sites*Sergei Noskov and Bogdan Lev*

Department of Biological Sciences, University of Calgary, Calgary, AB, Canada

A statistical-mechanical framework is presented to clarify the role of different contributions underlying the ion selectivity in protein binding sites. The relative free energy of bound ions is expressed in terms of a reduced subsystems helping to isolate the local degrees of freedom in the coordinating shell coupled to a potential of mean force representing the influence of the rest of the protein. The theoretical framework presented makes it possible to delineate two important limiting cases in selective cation binding to proteins. The theory is illustrated by studies of binding sites in the potassium channels and the sodium-selective transporters. The role of quantum effects and electronic polarization in monovalent cation binding to proteins is discussed based on recently developed QM/MM free energy simulations.

From Water Structure and Fluctuations to Hydrophobicity of Proteins and Interfaces*Shekhar Garde*

Chemical & Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY, USA

Water-mediated interactions (e.g., hydrophobic interactions) govern a host of biological and colloidal self-assembly phenomena from protein folding, and micelle and membrane formation, to molecular recognition. Macroscopically, hydrophobicity is often characterized by measuring droplet contact angles. Such measurements are not feasible for nanoscale surfaces of proteins or nanoparticles. How does one then characterize hydrophobicity/philicity of such interfaces? We present results from theory and simulations of hydration of a variety of surfaces to connect the behavior of water at the nanoscale interfaces and their hydrophobicity. Specifically, we show that water density fluctuations (and not the average local density) provide a quantitative characterization of the interface hydrophobicity. Density fluctuations are enhanced at hydrophobic interfaces and suppressed near hydrophilic ones. Simulations also show how properties of water at interfaces influence solute binding, folding, and dynamics of flexible molecules at interfaces. I will demonstrate that this new perspective on hydrophobicity provides a tool for characterization of hydrophobicity patterns on protein surfaces, which are relevant for binding, recognition, and aggregation. If time permits, I will tell a brief story about our upcoming IMAX movie, *Molecules to the MAX*.

Computer Simulations of Lipids

Peter Tieleman, Svetlana Baoukina and Drew Bennett

Department of Biological Sciences, University of Calgary, Calgary, AB, Canada

Computer simulation is a powerful method to study the properties of lipids in biological membranes. With increasing computer power and modern software sophisticated detailed models with thousands of lipids can be followed on time scales of hundreds of nanoseconds, while new coarse-grained methods can reach tens of microseconds on systems as large as vesicles. Biophysical and biochemical problems within reach include detailed free energy calculations on lipid-lipid interactions, membrane remodeling by proteins, pore formation due to electric fields or antimicrobial peptides, the details of monolayer compression, expansion, and breakdown, and direct simulation of protein-induced vesicle fusion. I will focus on two projects that illustrate the capabilities of computer simulations of lipids.

We investigated the thermodynamics of lipid-cholesterol interactions and calculated distributions and flip-flop rates for both lipids and cholesterol. Lipid flip-flop is slow on a physiological time scale. In contrast, cholesterol equilibrates rapidly between membrane leaflets with a strong dependence on lipid composition. Free energy calculations on cholesterol and the signaling lipid ceramide combined with large-scale equilibrium simulations are beginning to shed light on the thermodynamics of raft or nanoscale domain formation.

The coarse-grained MARTINI model is a useful approach to study large-scale phenomena such as monolayer behavior in models of lung surfactant. Lipid composition is a major determinant of the properties of lung surfactant, as are a number of surfactant proteins. Based on extensive simulations we show that a model of the surfactant protein SP-B induces spontaneous fusion between two vesicles in solution. SP-B also appears to be important for stabilizing vesicles attached to a monolayer when the monolayer is compressed beyond its limits and lipids are squeezed out of the interface.

References

1. W.F.D. Bennet, J.L. MacCallum, M. Hinner, S.J. Marrink, D.P. Tieleman. 2009. A molecular view of cholesterol flip-flop and chemical potential in different membrane environments, *J. Am. Chem. Soc.* **131**, pp. 12714-12720
2. S.J. Marrink, A.H. de Vries, D.P. Tieleman. 2009. Lipids on the move: simulations of membrane pores, domains, stalks and curves, *Biochim. Biophys. Acta* **1788**, pp. 149-168
3. S. Baoukina, L. Monticelli, J. Risselada, S.J. Marrink, D.P. Tieleman. 2008. The molecular mechanism of lipid monolayer collapse, *Proc. Natl. Acad. Sci.* **105**, pp. 10803-10808
4. S.J. Marrink, J. Risselada, S. Yefimov, D.P. Tieleman, A.H. de Vries. 2007. The MARTINI force field: coarse grained model for biomolecular simulations, *J. Phys. Chem. B.* **111**, pp. 7812-7824

O12

Hybrid Potential Simulations of Enzyme Catalysis

Martin Field

Institut de Biologie Structurale - Jean-Pierre Ebel, Grenoble, France

An important goal of computational and theoretical biochemistry is helping elucidate how enzymes achieve their catalytic efficiency. The extended nature of such systems, however, makes this a challenging task for simulation techniques. An approach that has proved particularly powerful for the investigation of enzymatic and other condensed phase reaction processes is the use of hybrid quantum mechanical and molecular mechanical potentials. This talk will highlight recent methodological developments aimed at increasing the precision and the utility of the hybrid potentials employed in the author's group. These improvements will be illustrated by a discussion of their application to specific enzyme systems.

Theoretical Studies of Enzymes

Walter ThielMax-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim,
Germany

Combined quantum mechanical/molecular mechanical (QM/MM) approaches have emerged as the method of choice for treating local electronic events in large molecular systems, for example, chemical reactions in enzymes or photoinduced processes in biomolecules. The lecture will outline the theoretical background and the commonly chosen strategies for QM/MM studies of biomolecular reactions [1,2] before addressing current methodological challenges [3-5]. In the second part, it will describe some of our recent work on biocatalysis by enzymes which includes mechanistic studies on cytochrome P450cam [6,7] and xanthine oxidases [8-11]. These studies have addressed, inter alia, the biocatalytic role of single water molecules, the competition between coupling and uncoupling reactions in the wild-type P450cam enzyme and its mutants, and the crucial role of active-site residues in the reductive half-reaction of xanthine oxidases. The examples presented will illustrate the chemical insights and the improved mechanistic understanding of enzymatic reactions that can be provided by QM/MM calculations.

References

- [1] H. M. Senn, W. Thiel, *Top. Curr. Chem.* **268**, 173-290 (2007).
- [2] H. M. Senn, W. Thiel, *Angew. Chem. Int. Ed.* **48**, 1198-1229 (2009).
- [3] R. A. Mata, H.-J. Werner, S. Thiel, W. Thiel, *J. Chem. Phys.* **128**, 025104 (2008).
- [4] H. M. Senn, J. Kästner, J. Breidung, W. Thiel, *Can. J. Chem.* **87**, 1322-1337 (2009).
- [5] T. Benighaus, W. Thiel, *J. Chem. Theory Comput.* **5**, 3114-3128 (2009).
- [6] M. Altarsha, T. Benighaus, D. Kumar, W. Thiel, *J. Am. Chem. Soc.* **131**, 4755-4763 (2009).
- [7] S. Shaik, S. Cohen, Y. Wang, H. Chen, D. Kumar, W. Thiel, *Chem. Rev.* **110**, 949-1017 (2010).
- [8] S. Metz, D. Wang, W. Thiel, *J. Am. Chem. Soc.* **131**, 4628-4640 (2009).
- [9] S. Metz, W. Thiel, *J. Am. Chem. Soc.* **131**, 14885-14902 (2009).
- [10] S. Metz, W. Thiel, *J. Phys. Chem. B* **114**, 1506-1517 (2010).
- [11] J. M. Dieterich, H.-J. Werner, R. A. Mata, S. Metz, W. Thiel, *J. Chem. Phys.* **132**, 035101 (2010).

Semiempirical Quantum Models for Metalloenzymes*Guillaume Lamoureux and Shihao Wang*

Department of Chemistry and Biochemistry and Center for Research in Molecular Modeling, Concordia University, 7141 Sherbrooke Street West, Montréal, Québec, H4B 1R6

We are developing site-specific semiempirical models for the simulation of chemical reactions in metalloenzymes. These models aim at reproducing the essential features of the reaction (relative energies of the reactants and products, activation energies, structure of the transition state, etc.) using high-level ab initio energy surfaces as reference data. Compared to conventional DFT-based QM/MM approaches, the computational speedup provided by semiempirical models allows to investigate the fate of the reactants over longer time scales and to tackle a greater diversity of enzymes. We will illustrate our modeling approach using zinc-containing metalloenzymes.

The Signature of Nonadiabatic Transitions on the Pump-Probe Infrared Spectra of a Hydrogen-bonded Complex Dissolved in a Polar Solvent*Gabriel Hanna*¹ and *Eitan Geva*²¹Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada²Department of Chemistry, University of Michigan, Ann Arbor, Michigan, USA

The mixed quantum-classical Liouville equation provides a unified and self-consistent platform for modeling the spectral signatures of nonequilibrium solvation dynamics, non-Condon effects, and nonadiabatic transitions. These features will be demonstrated in the context of the pump-probe infrared spectra of a hydrogen stretch in a moderately strong hydrogen-bonded complex dissolved in a polar solvent. Particular focus will be placed on incorporating nonadiabatic transitions and demonstrating their unique spectral signature.

Quantum Biology of Photosynthesis in Purple Bacteria*Klaus Schulten*

Theoretical and Computational Biophysics Group, Beckman Institute, University of Illinois
at Urbana-Champaign, Urbana, IL 61801, USA

Photosynthesis transforms the energy of sun light into chemical energy. One of the simplest realizations is found in so-called purple bacteria that build in their interior hundreds of 60 nm wide spherical membranes of lipids and proteins absorbing sun light and producing adenosine triphosphate from adenosine diphosphate. My group has described this photosynthetic membrane since over three decades, from light absorption through absorption by carotenoids and chlorophylls, 100 femtosecond electronic energy transfer between carotenoids and chlorophylls, picosecond equilibration into exciton states of coherently shared electronic excitations among clusters of chlorophylls, 10 picosecond exciton migration through the entire membrane including thousands of chlorophylls, and finally nanosecond electron transfer between redox groups in transmembrane proteins that charge the photosynthetic membrane. We also established the structural identity of the proteins organizing the light harvesting process in the photosynthetic membrane as well as how these proteins curve the membrane into its spherical shape. Lastly, we determined through electron microscopy and atomic force microscopy the overall architecture of the spherical photosynthetic membrane systems with their 200 proteins. The lecture will outline the multiscale approach taken to describe the overall photosynthetic membrane, starting with $T = 0$ quantum chemistry, continuing with finite temperature quantum chemistry coupling of electronic degrees of freedom to a bath of thermal oscillators, continuing with the use of dissipative quantum mechanics for an account of coherent and incoherent exciton migration, continuing further with classical molecular dynamics for the description of membrane shape, to finally invoke mathematical modeling that combines multi-modal experimental input into a consistent overall description of the organelle architecture. The lecture will also demonstrate how hundreds of proteins combine their properties to build the organelle in the bacterium, using the photosynthetic membrane as an example for the new field of systems biology.

Reaction Kinetics in Viscous Media: Molecular Dynamics and Stochastic Models

*Noham Weinberg^{1,2}, Jeffery Perkins¹, Liam Huber^{1,4}, Essex Edwards^{1,3}, Paul Dance¹ and
Melissa Prachnau¹*

¹Department of Chemistry, University of the Fraser Valley, 33844 King Rd, Abbotsford,
BC Canada V2S 7M8

²Department of Chemistry, Simon Fraser University, 8888 University Drive Burnaby, B.C.
Canada. V5A 1S6

³Department of Computer Science, University of British Columbia, 2329 West Mall,
Vancouver, B.C. Canada V6T 1Z4

⁴Department of Physics, University of British Columbia, 2329 West Mall, Vancouver, B.C.
Canada V6T 1Z4

Observed in a number of high pressure isomerization reactions, viscosity-induced solvent effects manifest themselves in a significant departure of the reaction kinetics from the trends that might have been expected on the basis of the transition state theory. These effects are associated with the significant anisotropy in characteristic times of the reaction and solvent systems. Nonviscous solvents are sufficiently fast and can instantly adjust to the evolution of the reaction system. However, if viscosity of a solvent is too high or reaction is too fast, a misfit develops between the solvent and solute (reaction system) and reaction rate decreases. Molecular dynamics and Monte Carlo simulations have increasingly become the tool of choice in studying dynamic effects of solvent on reactions and relaxation processes in solute; however, they will likely remain limited to relatively simple and fast solute systems in the foreseeable future. Much less computer-demanding stochastic models will therefore continue to serve as a valuable instrument in describing reaction kinetics in more complex cases. We discuss both alternatives and establish a linkage between them by introducing a molecular-dynamics-based definition of a solvent coordinate associated with a given reaction coordinate.

Correlated Dynamics of the Double Hydrogen Bonds of Adenine-Uracil Base Pairs in Solution

Oliver Kühn and Yun-an Yan

Institute of Physics, University of Rostock, D-18051 Rostock, Germany

Hybrid QM/MM molecular dynamics simulations have been carried out for the Watson-Crick base pair of 9-ethyl-8-phenyladenine and 1-cyclohexyluracil in deuteriochloroform solution at room temperature (1,2). Trajectories are analyzed putting special attention to the geometric correlations of the $N-H\cdots N$ and $N-H\cdots O$ hydrogen bonds in the base pair. It is found that hydrogen bond and $N-H$ lengths follow a simple empirical correlation based Pauling's valence bond order model.

In order to describe the IR line shape of the two NH-stretching vibrations, the correlation between their fundamental as well as first overtone transition frequencies and the hydrogen bond lengths is exploited. This correlation is established on the basis of representative snapshot potentials for which the stationary Schrödinger equation for the target vibrations is solved. Equipped with this information fluctuating transition frequencies can be determined rather efficiently along the QM/MM trajectory. Using IR line shape theory, the shapes fundamental NH-stretching bands are obtained in reasonable agreement with experiment (3). The limitations of a second-order cumulant expansion are discussed as well.

Finally, the dynamics of the two hydrogen bonds is scrutinized on the basis of pump-probe and two-dimensional (2D) IR spectroscopy. In particular the shape of the off-diagonal peaks in the 2D spectrum reveals clear signatures of positive correlation between the two stretching vibrations.

References

- (1) Y. Yan, G. M. Krishnan, O. Kühn, *Chem. Phys. Lett.*, **464** (2008) 230
- (2) Y. Yan, O. Kühn, in "Excited-State Hydrogen Bonding and Hydrogen Transfer" Ke-Li Han and Guang-Jiu Zhao (Eds.), John Wiley & Sons, 2010
- (3) S. Woutersen, G. Cristalli, *J. Chem. Phys.*, **121** (2004) 5381

Quantum Molecular Dynamics Studied with MCTDH: Applications to H_5O_2^+ and Malonaldehyde

*Hans-Dieter Meyer*¹, *Oriol Vendrell*¹, *Markus Schroeder*¹ and *Fabien Gatti*²

¹Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg Im Neuenheimer Feld 229, 69120 Heidelberg, Germany

²CTMM, Institut Charles Gerhardt, UMR 5253, CC 1501, Université Montpellier II, F-34095 Montpellier, Cedex 05, France

We discuss a full (15D) quantum simulation of the infrared absorption spectrum and dynamics of the protonated water dimer H_5O_2^+ — also known as Zundel cation — by the multiconfiguration time-dependent Hartree (MCTDH) method. For this we used a potential energy surface and dipole-moment surfaces recently developed by Bowman and collaborators.

The main features of the IR spectrum are explained and assigned. In particular a complicated doublet structure at about 1000 cm^{-1} , which was not understood, is explained as a Fermi-resonance structure involving the proton transfer motion and wagging motion (water pyramidalization). Also the couplings of various fundamental motions which shape the spectrum between 800 and 2000 cm^{-1} are explained and their spectral lines are assigned.

A picture of the cation arises in which the central proton motion determines the dynamics of various other modes, mostly water bending and water pyramidalization, and controls the switch between H_3O^+ - and H_2O -like structures. A very strong coupling between the motion of the central proton and the internal water bendings shifts the bending line to higher energies and makes it rather bright.

The IR-spectra of the isotopologues D_5O_2^+ , $\text{H}(\text{D}_2\text{O})_2^+$, $\text{D}(\text{H}_2\text{O})_2^+$ show very strong isotope effects. The intensities of several lines changes dramatically because they borrow their intensity by coupling to the central proton motion. Energy shifts due to deuteration modify these couplings.

The malonaldehyde molecule is a prototype for studying proton transfer within molecules. In contrast to the Zundel cation, where the use of curvilinear coordinates was essential, one can use here the much simpler rectilinear normal modes coordinates. The larger dimensionality (21D), however, makes the calculations more elaborate. We present our first results on the tunnelling energy split.

Quantum Transport and Quantum Information in Molecules

Koichi Yamashita

Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo,
Bunkyo-ku, Tokyo 113-8656, Japan

In my talk, I will discuss about our recent theoretical studies in the field of nanoscience, that is quantum transport and quantum information. Our research object is to develop new theoretical methods for quantitative understanding of interfacial electronic quantum transport and for potential applications of molecular qubits to quantum computing.

We have so far developed new ab initio nonequilibrium Green's function (NEGF) method for electron-transport calculations in nanoscale devices based on the "efficient molecular-orbital approach" [1, 3]. We also derived simple expressions for the conductance and the inelastic electron tunneling spectrum (IETS) based on the rigorous lowest-order expansion formalism [2]. In order to illustrate our method, we have performed calculations of inelastic transport in a linear gold atomic wire and a benzene-dithiol molecule both sandwiched between gold electrodes. The shapes of the IETS, the effect of the temperature, and of the symmetry of the IETS signals are analyzed in details [4].

We have been engaged in research on quantum computing using molecular internal degrees of freedom [5]. Molecule-laser interactions are local interactions. We found that non-local interactions enable us to manipulate the three types of states separately, and proposed a method of molecule control for the generation of the Bell state [6]. We also conducted numerical design of optimal laser pulses for the Deutsch-Jozsa algorithm using vibration/rotation modes in the electron ground state of closed-shell as well as open-shell molecules, and demonstrated that quantum computing using the vibration/rotation modes is highly promising [7]. The process of producing entanglement from a separable stage is a quantum process that is highly sensitive to time. With this in mind, we developed a new optimum control theory which is free from the end-point time restriction [8].

References

- [1] H. Nakamura and K. Yamashita, *J. Chem. Phys.* **125**, 194106 (2006).
- [2] H. Nakamura and K. Yamashita, *Nano. Lett.*, **8**, 6 (2008).
- [3] H. Nakamura, K. Yamashita, A. R. Rocha and S. Sanvito, *Phys. Rev. B* **78**, 235420 (2008).
- [4] H. Nakamura and K. Yamashita, in *Molecular Nano dynamics, Vol. II: Active Surfaces, Single Crystal and Single Biocells*, p. 357-399 (Ed. H. Fukumura, M. Irie, Y. Iwasawa, H. Masuhara, and K. Uosaki, WILEY-VCH, 2009).
- [5] S. Suzuki, K. Mishima, and K. Yamashita, *Chem. Phys. Lett.* **410**, 358 (2005); K. Mishima, K. Shioya, and K. Yamashita, *Chem. Phys. Lett.* **442**, 58 (2007); K. Mishima and K. Yamashita, *Int. J. Quant. Chem.*, **109**, 1827 (2009); *Chem. Phys.* **361**, 106 (2009).
- [6] K. Mishima and K. Yamashita, *Chem. Phys.* **342**, 141 (2007); *Chem. Phys.* **352**, 281 (2008)
- [7] K. Shioya, K. Mishima, and K. Yamashita, *Mol. Phys.*, **105**, 1283 (2007); K. Mishima, K. Tokumo, and K. Yamashita, *Chem. Phys.* **343**, 61 (2008); K. Mishima and K. Yamashita, *Chem. Phys.* **367**, 63 (2010)
- [8] K. Mishima and K. Yamashita, *J. Chem. Phys.* **130**, 034108 (2009); *J. Chem. Phys.* **131**, 014109 (2009).

Adaptive Multiscale Molecular Dynamics Simulations of Soft Matter*Steven O. Nielsen*¹, *Preston B. Moore*² and *Bernd Ensing*³¹Department of Chemistry, University of Texas at Dallas, 800 West Campbell Road,
Richardson, TX 75080²Department of Chemistry and Biochemistry, University of the Sciences in Philadelphia,
Philadelphia PA 19104³Van't Hoff Institute for Molecular Sciences, Universiteit van Amsterdam, Nieuwe
Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Understanding mesoscopic phenomena in terms of the fundamental motions of atoms and electrons poses a strong challenge for molecular simulation. This challenge is being met by multiscale modeling techniques that aim to bridge between the microscopic and mesoscopic time and length scales. In such techniques different levels of theory are combined to describe a system at a number of scales or resolutions. In adaptive hybrid simulations, the different levels are used in separate spatial domains, and matter can diffuse from one region to another with an accompanying resolution change. Until now, however, adaptive atomistic/coarse-grained (AA/CG) molecular dynamics simulations have had very limited applicability because the on-the fly CG-to-AA transformation is problematic in all cases with the exception of molecules with a single particle CG representation. Here, we solve this problem by combining a transitional healing region with a rotational dynamics of rigid AA fragments in the CG region. Error control is obtained by analysis of the AA/CG energy flow. We illustrate the method with adaptive multiscale simulations of liquid hexane and of a dilute polymer solution in a theta solvent.

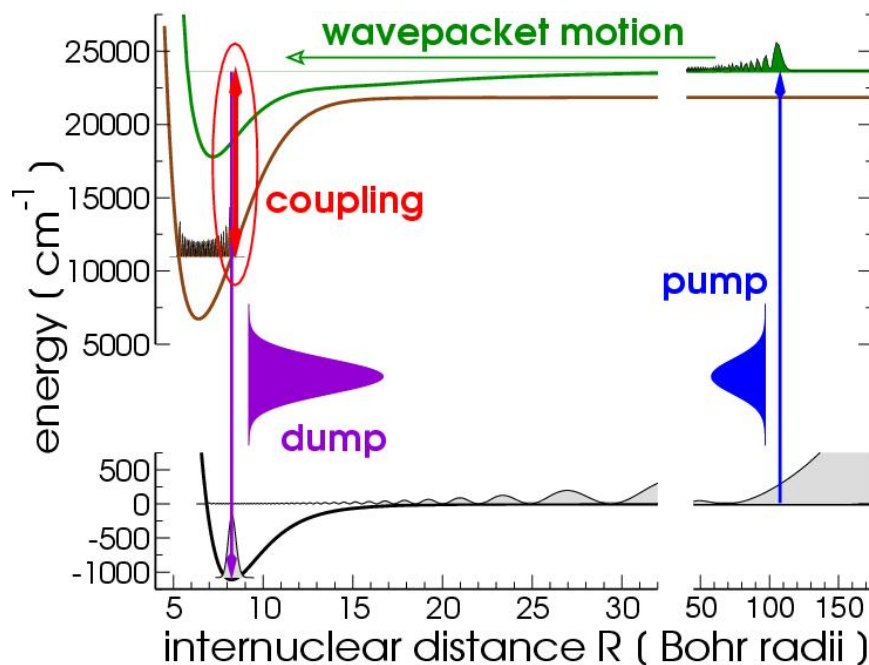
Coherent Control of the Photoassociation of Ultracold Molecules

Christiane Koch

Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

In photoassociation, two colliding atoms are excited by laser light to weakly bound levels of an electronically excited state. A pair of short laser pulses may be employed in a pump-dump sequence to produce ultracold molecules in their electronic ground state. Picosecond pulses turn out to be best suited based on the consideration of timescales, bandwidths and Franck-Condon factors.

The structure of ultracold molecules is precisely known, and their dynamics is very sensitive to small changes in this structure. This allows one to take the coherent control concept of shaping the potential energy surfaces which govern the dynamics literally: Resonances can be induced or possibly suppressed by external fields leading to a qualitative change of the dynamics.



Generally, coherent control has been extremely successful for destructive unimolecular processes such as ionization or dissociation but still remains an unresolved puzzle for associative binary reactions. The main difference between both processes lies in the initial states – a well-defined quantum state vs an incoherent continuum. At very low temperatures the interaction between atoms is solely determined by resonances and by tunneling, and the continuum structure can easily be manipulated by external fields. This paves the way toward improved controllability of associative processes, at least at very low temperatures.

Tunable Excitons in Ordered Arrays of Ultracold Molecules on Optical Lattices*Roman Krems, Felipe Herrera, Jesus Perez-Rios and Marina Litinskaya*

Department of Chemistry, University of British Columbia, Vancouver, Canada

We consider collective excitations of internal energy in ordered arrays of ultracold polar molecules trapped in an optical lattice. We demonstrate that an external dc electric field can be used to modify the dynamics of rotational excitons in an ensemble of closed-shell molecules and magnetic excitons in an ensemble of open-shell molecules in optical lattices. The systems proposed here may thus be used for time-domain quantum simulation of localization phenomena and spin excitation transfer in disordered media.

In particular, we show that a mixture of interacting ultracold polar molecules trapped in an optical lattice can be used to study controllable exciton-impurity scattering. We demonstrate that an external dc electric field can be used to induce scattering resonances in collisions of rotational excitons with impurities, which can lead to strong localization of excitons. On the other hand, a proper choice of the electric field can be used to induce delocalization of the eigenstates of the system due to the cancellation of the effects of diagonal and off-diagonal disorder. Consequently, by varying the potential strength as well as the concentration and distribution of impurities, it may be possible to realize different kinetic regimes of exciton dynamics, from free propagation to strong localization.

We also show that an ensemble of $^2\Sigma$ molecules on an optical lattice exhibits collective spin excitations that lead, at certain combinations of electric and magnetic fields, to the formation of a magnetic Frenkel exciton. We demonstrate that the dynamics of the magnetic Frenkel excitons can be tuned by varying both the electric and magnetic fields and that the exciton states can be localized by creating vacancies in the optical lattice. This can be exploited for engineering many-body entangled spin states with molecules. We explore the dynamics of magnetic exciton wavepackets and demonstrate that the spin excitation transfer between molecules in a finite-size molecular chain can be accelerated or slowed down by tuning an external magnetic or electric field.

Improving Reptation Quantum Monte Carlo*Stuart Rothstein^{1,3}, Wai Kong Yuen² and Daniel G. Oblinsky¹*¹Department of Chemistry, Brock University, St. Catharines, ON L2S 3A1 CANADA²Department of Mathematics, Brock University St. Catharines, ON L2S 3A1 CANADA³Department of Physics, Brock University St. Catharines, ON L2S 3A1 CANADA

In reptation quantum Monte Carlo (RQMC), one generates a large number of reptiles: sets of electron configurations arising from consecutive drift-diffusion moves. Within the fixed-node approximation, one extracts estimates of the exact energy from reptiles' heads and tails (their first and last configurations of electrons, respectively), and estimates expectation values for operators that don't commute with the Hamiltonian, from their middle configurations. An advantage over conceptually equivalent algorithms is that each estimate is free from population control bias. The time-step bias, however, may accumulate, adversely affecting one's ability to accurately estimate physical properties of atoms and molecules. For this purpose we propose alternative RQMC algorithms, engineered to remedy this deficiency, while still simulating the target distribution for RQMC. The effectiveness of our approach is demonstrated by an application to ground-state LiH and water. We estimate the fixed-node energy and non-energy-related properties with improved reliability.

DFT - Koopmans' Theorem

*Kimihiko Hirao*¹, *Takao Tsuneda*², *Jong-Won Song*³ and *Satoshi Suzuki*³

¹RIKEN, 6th Fl., Meiji Seimei Kan 2-1-1, Marunouchi, Chiyoda, Tokyo, Japan

²RIKEN, Wako, Saitama 351-0198, Japan

³University of Tokyo, Hongo, Bunkyo, Tokyo, Japan

MO is the most fundamental quality in quantum chemistry. Almost all of our understanding of “what the electrons are doing in molecule” is based on the MO concept. The success of Hartree-Fock method in describing the electronic structure has made it natural to analyze the wave function in terms of the MOs. The concept is simple and has a close relation to experiment through Koopmans' theorem.

In DFT a similar theorem exists that relates the first ionization energy and electron affinity to the HOMO and LUMO energies. While these are exact statements in the formalism of DFT, the use of approximate exchange-correlation potentials makes the calculated energies approximate.

In my talk I will demonstrate that our long-range corrected (LC) functionals satisfy DFT - Koopmans' theorem both for HOMO and LUMO. The reason why LC-DFT gives orbital energies quantitatively will also be discussed.

First-Principles Simulations of Tribological Processes*Nicholas Mosey*

Department of Chemistry, Queen's University, Kingston, ON, Canada K7L 3N6,
nicholas.mosey@chem.queensu.ca

Friction and wear are ubiquitous phenomena that have significant environmental and economic impacts. For example, the annual costs associated with energy losses due to friction and the need to prematurely replace worn out equipment are estimated to be several percent of the GDP in industrialized nations. Furthermore, energy losses due to friction place additional demands on finite energy resources. In order to more effectively control friction and wear, it is necessary to have a better understanding of the processes that occur in sliding contacts. First-principles chemical simulation can play a key role in this respect, offering insight into the details of these processes at the atomic and electronic levels, and providing a means of characterizing the extreme conditions experienced in sliding contacts.

In this presentation, I will discuss our efforts to study lubricated sliding contacts through first-principles molecular dynamics simulation. Emphasis will be placed on two areas. First, I will discuss our recent exploration of sliding interfaces composed of hydroxylated surfaces. This work has shed light on how chemical interactions between sliding surfaces affect friction, and led to a predictive model that accounts for experimentally-observed deviations from Amontons' basic law of friction arising from these interactions. The development of such a model is a significant advancement in the basic understanding of friction. Second, I will discuss work aimed at using the extreme conditions experienced in sliding contacts to transform simple molecules into effective lubricants. Specifically, I will show how compression and shear can transform aldehydes into polyethers, which are known to be good lubricants. We suggest that reactions of this type could form the basis of a new approach to lubrication in which lubricant molecules actively adapt to the conditions experienced in contacts instead of merely acting as passive mechanical boundaries between sliding surfaces.

Advances in the Simulation of Nanoporous Materials for Carbon Dioxide Capture*Tom Woo*

Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa

Carbon dioxide sequestration and storage (CSS) represents a serious strategy to reduce greenhouse gas emissions. CSS involves scrubbing CO₂ from a generating source, such as a coal burning plant, and permanently storing it. Currently, large scale CCS is not practical because the technologies to scrub CO₂ in an energy effective manner has not been developed. Recently, nanoporous metal organic frameworks (MOFs) materials have gained significant attention as the possible basis for new low energy CO₂ capture technologies. Our group's recent advances in simulating the selective gas adsorption by nanoporous materials will be presented. This includes the first method to derive electrostatic potential fitted atomic charges from periodic electronic structure calculations that we have termed REPEAT. The REPEAT charges have allowed us to accurately reproduce the experimental gas adsorption isotherms of a variety of different MOF materials. Moreover, to the best of our knowledge we are the first to confirm that molecular simulation is also able to reproduce the experimentally determined binding sites of CO₂ in MOFs. Our efforts to develop a high throughput computational screening methodology to aid in the engineering of new materials will also be presented.

Interacting Electrons Confined in Cavities of Almost Arbitrary Shape*Viktor N. Staroverov and Ilya G. Ryabinkin*Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7,
Canada

We present a method of solving the Schrödinger equation for two interacting electrons confined in an almost arbitrary infinite-potential well of axial symmetry. Using this method we obtain full configuration interaction solutions for two electrons in a sphere, a cylinder, a bulged cylinder, a capsule, and a “dogbone” (two spherical cavities connected by a channel). We find that among all cavities of equal volume, spherical confinement is optimal for small volumes; for large volumes, the capsule-shaped system has a significantly lower energy. The magnitude of the singlet-triplet gap strongly depends on the shape of the cavity and, for a fixed volume, decreases in the following order: bulged cylinder, sphere, cylinder, capsule. For a dogbone-shaped cavity, the singlet-triplet gap increases with increasing diameter of the connecting channel, but shows weak dependence on the channel’s length. These results account for the observed magnetic properties of electrides - ionic solids in which almost-free electrons move in a network of cavities and channels formed by the cationic lattice.

Correlation from the Electron Pair Perspective

Jason Pearson and Adam Proud

Department of Chemistry, University of Prince Edward Island, Charlottetown, PE, Canada

The correlation problem remains as one of the most significant challenges in quantum chemistry. Methods capable of accurately capturing correlation energies that are computationally and conceptually simple (at least relative to sophisticated post-HF methods) would revolutionize our discipline yet remain decidedly elusive. Although there are many promising candidates being developed to this end [1], we would propose that a sound understanding of the phenomenon of correlation and its effects is likely to be fruitful in the search for revolutionary correlation models. This doctrine has guided the pioneering work of Coulson and Neilson [2] in the study of electron pair distributions, now known as intracules. Intracules describe the probability distribution for the interelectronic separation of electron pairs in atomic and molecular systems and have been particularly popular among Canadian theoreticians [3]. Because the electron pair density provides detailed information about interactions between electrons it is a valuable quantity to study, yet is difficult to analyze directly because of its topological complexity and thus intracules offer a feasible alternative. Analogous to intracules are extracules, which are the probability densities for the centre of mass of an electron pair. These densities have been utilized extensively for the purposes of investigating correlation effects in atoms and molecules but more generally for studying fundamental electron-electron interactions in ways that the conceptually more simple electron density, $\rho(r)$, simply does not allow [4].

In this presentation I will describe the accuracy of new intracule functional models for capturing the electron correlation energy [5] and discuss the effects that correlation induces in such distributions [6]. I will also outline a new probability density for describing correlation effects in atomic and molecular systems, the intex density.

References

- [1] C. D. Sherrill, *J. Chem. Phys.* **132**, 110902 (2010)
- [2] C. A. Coulson and A. H. Neilson, *Proc. Phys. Soc. (London)* **78**, 831 (1961)
- [3] See, for example, A.J. Thakkar, V.H. Smith Jr., *Chem. Phys. Lett.* **42**, 476 (1976); A.J. Thakkar, A.N. Tripathi, V.H. Smith Jr., *Int. J. Quantum Chem.* **26**, 157 (1984); R.J. Boyd, C.A. Coulson, *J. Phys. B* **6**, 782 (1973); X. Fradera, C. Sarasola, J.M. Ugalde and R.J. Boyd, *Chem. Phys. Lett.* **304**, 393 (1999)
- [4] J. Cioslowski and G. Liu, *J. Chem Phys.* **105**, 8187 (1996)
- [5] J.K. Pearson, D.L. Crittenden and P.M.W. Gill, *J. Chem. Phys.* **130**, 164110 (2009)
- [6] J.K. Pearson, P.M.W. Gill, J.M. Ugalde, and R.J. Boyd, *Mol. Phys.* **107**, 1089 (2009)

Theoretical Chemistry in Canada: A Personal Perspective

Russell Boyd

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

I will present a personal perspective on the development of theoretical and computational chemistry in Canada during the past forty years. Some of the pioneers and their seminal contributions will be used to illustrate Canada's strong tradition in theoretical and computational chemistry. Furthermore, I will attempt to comment on the current state of theoretical and computational chemistry in Canada and I will speculate on some of the current challenges and opportunities.

The Role of Solvent Polarization in the Spectroscopy of the Hydrated Electron*John Herbert and Leif Jacobson*Department of Chemistry, The Ohio State University, 100 W. 18th Ave., Columbus, OH
43210

The aqueous electron (e_{aq}^-) and its finite analogues, the anionic water clusters $(\text{H}_2\text{O})_N^-$, have attracted significant attention from both theory and experiment for several decades. Nevertheless, some of the most basic structural aspects of these systems, as well as the interpretation of certain spectroscopic features, remain controversial or else have defied theoretical explanation altogether. This talk will describe our efforts to develop a one-electron pseudopotential model for mixed quantum/classical molecular dynamics simulations of the hydrated electron, in which many-body electron-water and water-water polarization are treated in a fully self-consistent fashion. This model is quantitatively accurate, as compared to *ab initio* benchmarks for clusters ranging in size from $N = 2 - 33$, but is affordable enough to be used in bulk simulations with periodic boundary conditions. We find that self-consistent polarization is *qualitatively* important for describing the electronic and photoelectron spectroscopy of (e_{aq}^-) in bulk water. In particular, these are the first calculations that successfully reproduce the “blue tail” in experimental electronic absorption spectrum. We attribute this tail to quasi-continuum states that are bound only by solvent polarization upon electronic excitation.

Time-Dependent Density Functional Theory for Open Quantum Systems and Its Linear-Response Implementation

Alán Aspuru-Guzik¹, David Tempel², Joel Yuen-Zhou¹ and Cesar Rodriguez-Rosario¹

¹Department of Chemistry and Chemical Biology, Harvard University

²Department of Physics, Harvard University

The Casida equations of linear response TDDFT are extended to calculate linear spectra of open quantum systems evolving according to a Markovian master equation. By mapping a many-body open quantum system onto an open, non-interacting Kohn-Sham system, extrinsic line broadening due to electron-bath coupling can be described exactly within TDDFT. The structure of the resulting matrix equations are analyzed for the generic case of electrons linearly coupled to a harmonic bath within Redfield theory. An approximate form of the exchange-correlation kernel based on first-order Goerling-Levy perturbation theory is derived.

The results presented here pave the way for intrinsically-line broadened and shifted spectra for a TDDFT that includes dissipation effects and complement our early work on TDDFT for open systems where we proved the theorems for a general Non-Markovian case.

I will present results of our early numerical simulations of the system on small and medium-size molecules.

References

Theory of Excitation Broadening using Time-Dependent Density Functional Theory for Open Quantum Systems. David G. Tempel and Alán Aspuru-Guzik. Submitted (2010). Preprint Available at arxiv:1004.0189

Time-Dependent Density Functional Theory for Open Quantum Systems with Unitary Propagation. Joel Yuen-Zhou, David Tempel, César Rodríguez-Rosario and Alán Aspuru-Guzik. *Physical Review Letters* **104**, 043001 (2010).

Time-dependent current-density functional theory for generalized open quantum systems. Joel Yuen-Zhou, César Rodríguez-Rosario and Alán Aspuru-Guzik. *Physical Chemistry Chemical Physics*, **11**, 4509, (2009)

Toward Accurately Predictive Quantum Chemistry with the Solutions of the Schrödinger and Dirac-Coulomb Equations

Hiroshi Nakatsuji

Quantum Chemistry Research Institute, JST CREST, Kyodai Katsura Venture Plaza
North, Goryo Oohara 1-36, Nishikyo-ku, Kyoto 615-8245, Japan

We have proposed the free complement (FC) method to solve the Schrödinger and relativistic Dirac-Coulomb equations very accurately for atoms and molecules. The FC method is based on the considerations on the structure of the exact wave function and on the introduction of the scaled Schrödinger equation to avoid the singularity problem caused by the Coulomb potential included in the Hamiltonian of atoms and molecules. The FC wave function, which is potentially exact, is generated from some adequate initial function automatically with the use of the Hamiltonian and the scaling function. All we have to do is to optimize the linear coefficients involved in the FC wave function with the use of the variation principle or the local Schrödinger equation (LSE) principle. We can obtain highly accurate wave functions of atoms and molecules with this methodology for both ground and excited states. The same is true for solving the Dirac-Coulomb equation. In comparison with the existing quantum chemistry method, the present method is basis-set free and so does not have “basis-set nightmare”. It is characterized by its analytical formulation.

We can reach the non-relativistic Schrödinger limit, relativistic Dirac-Coulomb limit, and so it is important to examine the amount of quantum electro-dynamic (QED) effect and even the rest, if it exists. This is true even when the system is in a very strong magnetic field.

For few electron systems, for which the integrals of the complement functions can be calculated analytically, we can reach the non-relativistic Schrödinger limit and the relativistic Dirac-Coulomb limit. The FC method has reproduced up to the three to five digits of the experimental excitation energies of a few electron atoms. High accuracy of the calculated wave function was also confirmed by examining local energy, cusp values, etc.

For many electron systems, we use the integral-free LSE method. Recently, we have developed the efficient and transferable rational sampling method, an efficient antisymmetrization method, and from atom to molecule (FATM) method, which are computationally less demanding. We hope, toward accurate and predictive quantum chemistry, these recent developments may open a way for doing chemistry with the solution of the Schrödinger equation and Dirac-Coulomb equation.

The Accuracy of the Pseudopotential Approximation*Peter Schwerdtfeger*

The New Zealand Institute for Advanced Study, Massey University, 0745 Auckland, New Zealand

The treatment of atoms and molecules with a large number of electrons still remains a challenge to quantum chemists since Hartree-Fock (HF) or density functional theory (DFT) based procedures scale generally like Nm , with N being the number of basis functions involved. Even with the exponential increase in CPU power of computers over the last decades, which at the turn of the century reached the tera-flop region in performance, and the introduction of sophisticated algorithms and approximations to HF, post-HF and DFT methods, which can in some cases yield an almost linear scaling in computer time with increasing number of atoms, for large and heavy molecules there is still a need for further approximations without significant loss of accuracy for the calculated properties of interest. Such an approximation is the pseudopotential approximation (PPA), also called effective core potential method (ECP), originally introduced by Hans G. A. Hellmann in 1934 as combined approximation method (kombiniertes Näherungsverfahren). The PPA applies the chemist's very basic idea that only valence electrons are important for the understanding of chemical bonding and processes. And relativistic effects can easily be implemented in an economic way into the PPA. This talk gives an overview on current pseudopotential schemes and their performance compared to all-electron calculations.

Heavy Elements' Chemistry with Relativistic Model Core Potential and Recent Large-scale Molecular Theory

Hirotohi Mori

Ocha-dai Academic Production, Division of Advanced Sciences, Ochanomizu University,
2-1-1 Ohtsuka, Bunkyo-ku, Tokyo 112-8610, Japan

In the last two decades, we have developed non-relativistic and relativistic model core potentials (MCPs) accompanied by valence functions for atoms up to Rn [1-5]. The MCP method, as well as the ab initio model potential (AIMP) method by Seijo *et al.* [6-9], is based on the theory proposed by Huzinaga *et al.* and has the advantage of producing valence orbitals with nodal structures over various other effective core potential (ECP) methods. The nodeless pseudo-orbitals in the usual ECP approaches may produce a large exchange integral and thus overestimate the correlation energies, resulting in excessive singlet-triplet splittings, for example [10,11]. On the other hand, the valence orbitals with a nodal structure in the MCP and AIMP methods can describe the valence correlation effects with reasonable accuracy. We have shown for main group elements that the valence correlation effects can be described adequately by a combination of split MCP valence orbitals and correlating contracted Gauss type functions.

We recently developed new MCP basis sets (spdsMCP) for the transition metal atoms, where (n-1)s, (n-1)p, (n-1)d and ns electrons ($n = 4, 5, 6$ for 1st, 2nd and 3rd transition metals) are treated explicitly [12-14]. These MCP data can be found on-line basis sets database, <http://setani.sci.hokudai.ac.jp/sapporo/Order.do>. MCP integral and its analytical derivative have already implemented in some quantum chemical program packages, GAMESS, ABINIT-MPX, and MOLCAS. In this presentation, I'll introduce the MCP theory and discuss the applicability to heavy elements' chemistry by showing some application results containing not only small diatomic molecules but also large scale nano/bio-systems containing heavy metal elements.

References

- [1] Y. Sakai, E. Miyoshi, M. Klobukowski and S. Huzinaga, *J. Comput. Chem.* **8** (1987) 226.
- [2] Y. Sakai, E. Miyoshi, M. Klobukowski and S. Huzinaga, *J. Comput. Chem.* **8** (1987) 264.
- [3] Y. Sakai, E. Miyoshi, M. Klobukowski and S. Huzinaga, *J. Chem. Phys.* **106** (1997) 8084.
- [4] E. Miyoshi, Y. Sakai, K. Tanaka and M. Masamura, *J. Mol. Struct.: Theochem* **451** (1998) 73.
- [5] Y. Sakai, E. Miyoshi and H. Tatewaki, *J. Mol. Struct.: Theochem* **451** (1998), 143.
- [6] S. Huzinaga, L. Seijo, Z. Barandiaran and M. Klobukowski, *J. Chem. Phys.* **86** (1987), 2132.
- [7] L. Seijo, Z. Barandian and S. Huzinaga, *J. Chem. Phys.* **91** (1989) 7011.
- [8] Z. Barandiran, L. Seijo and S. Huzinaga, *J. Chem. Phys.* **93** (1990), 5843.
- [9] Z. Barandiaran and L. Seijo, *Can. J. Chem.* **70** (1992) 409.
- [10] B. Pittel and W.H.E. Schwartz, *Chem. Phys. Lett.* **46** (1977) 121.
- [11] C. Teichteil, J.P. Malrieu and J.C. Barthelat, *Mol. Phys.* **33** (1977) 181.
- [12] Y. Osanai, M. S. Mon, T. Noro, H. Mori, H. Nakashima, M. Klobukowski, and E., Miyoshi, *Chem. Phys. Lett.* **452**, 210 (2008).
- [13] Y. Osanai, E. Soejima, T. Noro, H. Mori, M. S. Mon, M. Klobukowski, and E. Miyoshi, *Chem. Phys. Lett.* **463**, 230 (2008).
- [14] H. Mori, K. Ueno-Noto, Y. Osanai, T. Noro, T. Fujiwara, M. Klobukowski, and E. Miyoshi, *Chem. Phys. Lett.* **476**, 317 (2009).

Design of DANA-based Inhibitors of the Mammalian Neuraminidase, NEU3

*Amgad Albohy, Yao Zou, Matthew Li, Ruixiang Blake Zheng, Chunxia Zou and
Christopher W. Cairo*

Alberta Ingenuity Centre for Carbohydrate Science, Department of Chemistry, University of Alberta, Edmonton Alberta T6G 2G2, Canada

The human neuraminidase 3 (NEU3) is a membrane-associated sialidase that is responsible for the hydrolysis of terminal sialic acid residues of glycolipids. It has been proposed that NEU3 plays an important role in cell-cell interactions and in the control of cell signaling processes, such as apoptosis. Recently, overexpression of NEU3 has been linked to colon cancer, highlighting the need for a better understanding of the function of this enzyme.

Since NEU3 has not yet been studied by X-ray diffraction, we built a homology model of NEU3 based on the reported NEU2 crystal structure, using MODELLER (PDB ID: 1VCU). Docking calculations were performed using Autodock. From these studies we generated a model of 2,3-dehydro-3-deoxy-N-acetylneuraminic acid (DANA), a known inhibitor, and GM3, a lipid substrate, bound to NEU3. Multiple NEU3 site directed mutants were generated in order to study the mechanism and interactions between the enzyme and inhibitors. The kinetics of the generated mutants were determined and compared with the wild type enzyme. Additionally, the IC₅₀ of DANA was also measured for several mutants. The mechanism of NEU3 hydrolysis was found to be that of a retaining sialidase using NMR. The effect of different additives on the activity of NEU3 was also studied, and it was found that divalent cations, such as calcium, did not have a significant effect on activity.

Examination of the docked model of DANA in the active site of NEU3 suggests that there is a large hydrophobic pocket around the glycerol side chain of the inhibitor. This pocket is not present in NEU2, and could therefore be used for the design of selective inhibitors of NEU3. Another remarkable point in the docked structure of DANA is that the pocket of the 5-N-acetyl side chain is very small. Several DANA derivatives at these two positions were synthesized and their IC₅₀ values were measured. Two of the glycerol side chains derivatives showed better inhibition for NEU3 over the original inhibitor, DANA.

A2

Binding Energies of Fe(III) with Ligands Relevant to Alzheimer's Disease: An *ab Initio* Study

Jorge Ali-Torres and Arvi Rauk

Department of Chemistry, University of Calgary, Calgary, AB, T2N 1N4: rauk@ucalgary.ca

Alzheimer's disease (AD) is the most common form of neurodegenerative dementia. It is well known that some biological available metals, like copper, zinc and iron, interact with the amyloid beta peptide ($A\beta$). The role of copper ions has been studied extensively and is reasonably well understood.[1,2] However, the role of iron, one of the most abundant metals in biological systems, and highly redox active, has not been widely investigated in the context of $A\beta$ and Alzheimer's disease.

In this study we apply *ab initio* computational methodology to calculate binding energies of Fe(III) with some important relevant ligands in AD: methylimidazole (a model for His), phenol (a model for Tyr), acetate (a model for Glu and Asp) and the HisHis dipeptide (a model for the H1s13His14 region of $A\beta$). The calculated Raman spectra of some of the iron complexes will be also presented and compared to experimental data.[3]

[1] D. Raffa, G. A. Rickard, and A. Rauk. *J. Biol. Inorg. Chem* 2007, **12**, 147-164.

[2] N. Hewitt and A. Rauk. *J. Phys. Chem. B* 2009, **113**, 1202-1209.

[3] T. Miura, K. Suzuki, H. Takeuchi. *J. Mol. Struct.* 2001, **598**, 79-84.

A3

Phenomenological Models of Freezing in Gold Nanoparticles

Cletus Asuquo and Richard K. Bowles

Chemistry Department, University of Saskatchewan, Saskatoon, S7N5C9, Canada

Constrained Monte Carlo simulation is used to calculate the free energy barrier associated with the freezing of a 456-atom gold nanoparticle as a function of the solid embryo size and the distance of the embryo from the center of the cluster. This shows that freezing starts at the surface and the embryo grows inward. Different phenomenological models of nanoparticle freezing are then tested against our simulation data. The results suggest that the line tension, related to the three phase contact line, makes an important contribution to the free energy barrier.

Effects of Temperature on the Binding Interactions and Collective Dynamics of p53-DNA: Comparing the Wild-type to the R248Q Mutant

*Khaled Barakat*¹, *Bilkiss Issack*^{3,4,5}, *Maria Stepanova*^{4,5} and *Jack Tuszynski*^{1,2}

¹Department of Physics, University of Alberta, Edmonton, AB, Canada

²Department of Oncology, Cross Cancer Institute, Edmonton. AB, Canada

³Department of Electrical and Computer Engineering, University of Alberta, Edmonton, AB, Canada

⁴Department of Computing Sciences, University of Alberta, Edmonton, AB, Canada

⁵National Institute for Nanotechnology NRC, University of Alberta, Edmonton, AB, Canada

The protein p53, known as the guardian of the genome, plays an active role in the regulation of cell cycles. In about half of human cancers, the protein is inactivated by mutations located primarily in the DNA-binding core domain of the protein. More than 1300 distinctive carcinogenic single amino-acid alterations in the core domain of the protein have been reported. Of these, the R248Q and R248W mutants are most frequently encountered in human cancers. Experiments have revealed that the mutation of R248, among others, possesses temperature-induced DNA-binding characteristics.[1] In particular, R248-p53 mutant was defective for binding to DNA at 37C although it was able to bind specifically to several p53 response elements at sub-physiological temperatures (25 to 33C). The rescue of DNA-binding and subsequent restoration of activity in mutant p53 is becoming an increasingly popular strategy in developmental cancer therapy. The viability of the approach relies on designing small molecule drugs that reactivate p53 mutants upon binding and requires a thorough understanding of both the effects of p53 mutations and the molecular basis of the resulting inactivation.

In the present work, we focus on the temperature-induced structural changes to the wild-type core domain following the R248Q mutation. The effect of temperature on p53 proteins is investigated at the molecular level through their DNA-binding affinity and at the coarse-grained level through their collective dynamics. Molecular dynamics simulations were performed on models of the wild-type and mutant p53-DNA complex at four different temperatures, namely, 27C, 32C, 37C and 39C. Binding free energies were computed for the complexes at each temperature and decomposed into contributions from individual residues in order to characterise regions sensitive to binding. The conformational dynamics of p53 were analysed with a recently developed approach based on the collective dynamics of proteins. [2,3] Clustering of essential coordinates, determined from principal component analysis on the trajectories, indicate that structural domains of p53 are largely preserved in R248Q p53 below 37C. The flexibility profiles of the proteins reveal an increased flexibility of the L1 loop. When combined with insight from binding energy calculations, this suggests a potential route for the impaired activity of wild-type and p53 mutant at high temperatures.

[1] Friedlander P, Legros Y, Soussi T and Prives C, J. Biol. Chem. 271, 25468 (1996).

[2] M. Stepanova, Phys. Rev. E, 76, 051918 (2007).

[3] N. Blinov, M. Berjanskii, D. S. Wishart and M. Stepanova, Biochemistry 48, 1488 (2009).

A5

Constructing Profile Functions Spanning a Growing Solid/Liquid Molecular Interface

Eric Beaudoin, Payman Pirzadeh and Peter Kusalik

Department of Chemistry, University of Calgary

In simulations of crystal growth it is important to monitor the values of variables (e.g. energy, density, ...) along the direction of growth (z-axis) to see how those variables behave through the interfacial region. For small systems the plot of those variables versus z are noisy. Smoother plots can be achieved by averaging many such curves corresponding to different times. Prior to averaging the curves it is necessary to register the curves, i.e. shift them along the z -axis so that the solid/liquid interfacial region of each curve correspond to the solid/liquid interfacial region of every other curve. The uncertainty of the registration should be as small as possible. If the uncertainty is large, say about half the distance between the crystal layers, then the average of the density curve will be problematic because of destructive interference. A simple curve registration algorithm with small uncertainty based solely on the z -coordinate of the molecules is presented. The algorithm is applied to a system simulating the crystal growth of ice from liquid water.

Self-Assembly in Model Metal-Organic Framework Systems: A MD Simulation Study

Debasmita Biswal and Peter Kusalik

Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, AB, T2N1N4, Canada

Metal-organic frameworks (MOFs) are one-, two- or three-dimensional microporous crystalline materials that are immensely important for applications in gas-adsorption, storage and separation. Transition metal ions serve as the metal “connectors” that are bridged by rigid organic molecules, the “linkers”. Although a large number of experimentally synthesized MOFs can be found in literature, any detailed theoretical investigation for the pathway and mechanism of formation of these MOFs is currently lacking. The formation of MOFs involves the interplay between kinetics and thermodynamics, with solvent molecules possibly playing a major role. An analysis of the formation of model MOF systems through molecular dynamics (MD) simulation can aid our understanding of the intricate self-assembly processes involved therein, and might be used in the designing of new materials. In our preliminary studies, we have started with simple models representing metal centers, organic connectors, and solvent molecules. Our initial results show that formation of these MOFs is achievable with appropriate parameterization of these simple models. The proximity of two positively charged, heavy metal ions as metal ion pairs in the MOF structures seems to be one of the most intriguing phenomenon. Our analysis explores different pathways leading to formation of metal ion pairs held close together by the bridging organic linkers. Moreover, we also show that different MOF structures can be obtained by exploring the structural parameter space.

A7

How Many Intramolecular Hydrogen Bonds Does the Oxalic Acid Dimer Have?

Shamus A. Blair and Ajit J. Thakkar

Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick,
Canada E3B 5A3

Second-order Møller-Plesset (MP2) calculations are used to locate 69 unique minima on the potential energy surface of the oxalic acid dimer [1]. Additional MP2 calculations, with and without scaling of the spin components of the correlation energy, are performed for 24 selected minima using larger basis sets [2]. The global minimum is a dimer in which one of the monomers is not in its lowest-energy rotameric form. The dimer has two intermolecular and three intramolecular hydrogen bonds.

References

- [1] S.A. Blair, M.Sc. thesis, University of New Brunswick, 2007.
- [2] S.A. Blair and A.J. Thakkar, Chem. Phys. Lett., submitted (2010).

Electronic and Nuclear Fluxes During Pericyclic Reactions: Quantum Simulations for the Cope Rearrangement of Semibullvalene

*Timm Bredtmann*¹, *F. Marquardt*², *D. Andrae*¹, *I. Barth*¹, *H.-Ch. Hege*², *J. Manzt*¹ and *B. Paulus*¹

¹Institut für Chemie und Biochemie, Freie Universität Berlin, 14195 Berlin, Germany

²Visualization and Data Analysis, Zuse Institut Berlin, 14195 Berlin, Germany

Rules of organic chemistry describe the electronic flux during pericyclic reactions by Lewis structures of the reactants and rearrangement of neighboring bonds; this is graphically symbolized by curved arrows as shown in Fig. 1 for the degenerate Cope rearrangement of Semibullvalene (SBV). Despite the indisputable success of these rules for chemical synthesis, several questions remain: How many electrons actually flow, in which direction, and on which time scale? Which orbitals are involved?

Here, we use a general quantum method, recently developed in [1], in order to calculate the simultaneous fluxes of the coupled nuclei (F_{nuc}) and electrons (F_{el}) during the degenerate Cope rearrangement of SBV. This new approach combines the fields of quantum chemistry for stationary molecular properties and quantum reaction dynamics for electronic and nuclear fluxes leading to the following surprising answers:

The Cope rearrangement of SBV proceeds in the realm of femtochemistry. The numbers of electrons flowing from one side of SBV to the other in so called pericyclic orbitals (i.e. those related to bond pattern differences between the Lewis structures of the reactants and products), other valence orbitals, and core orbitals are, respectively, 0.4, 0.6, and 1.9, whereas the rules based on Lewis structures lead to the numbers 2, 0, and 0.

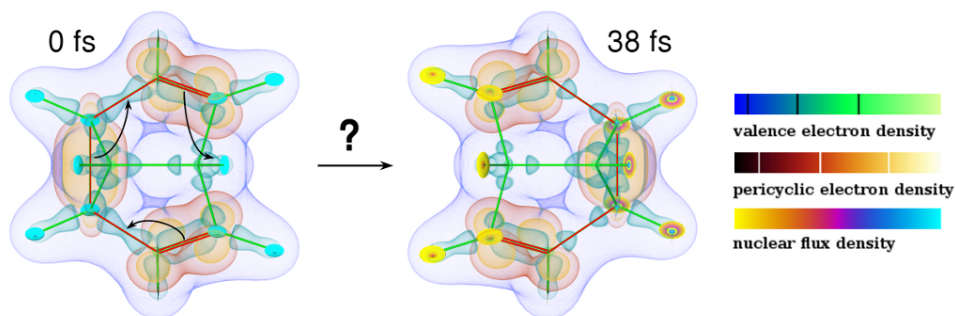


Figure 1 — Time evolution of the nuclear flux densities, and of the nuclear and electronic densities (valence density plus pericyclic density, see text), during Cope rearrangement of Semibullvalene (SBV), from the reactant ($t = 0$ fs) to the product ($t = 38$ fs). The vertical lines in the color maps indicate the chosen color for the isosurfaces for the valence- and pericyclic density.

[1] Barth, I.; Hege, H.-Ch.; Ikeda, H.; Kenfack, A.; Koppitz, M.; Manzt, J. Marquardt, F.; Paramanov, G.; *Chem. Phys. Lett.* **2009**, 481, 118

DFT Guided Monte Carlo Simulations: Application to Na₁₃ Cluster*Satya Bulusu and Rene Fournier*

Department of Chemistry, York University, Toronto, Ontario, Canada M3J1P3

We present a method by which a simple energy function gets fitted automatically to energies and gradients extracted from DFT calculations of structures generated during a Monte Carlo (MC) simulation. The fitness of energy function gets tested periodically using Classical Importance Function technique.[1] The function gets updated to fit the DFT energies and gradients of most recent structures visited if it has not achieved required fitness. In this way we can break down the global potential energy surface (PES) into small local regions and make the function work correctly for the particular local region rather than try to fit the function for the complete PES.

The method is applied for studying the PES of Na13 cluster. The energy function used here is Scaled Morse Potential (SMP)[2] fitted to DFT PBE calculations as implemented in ADF code. In a typical run at 150K for Na13, the total number of DFT energy evaluations required to run a million MC steps is nearly 6000. It means that that the DFT energy is evaluated only once for every 170 SMP energy evaluations. Metropolis MC simulations are performed at different temperatures to obtain thermodynamical values such as heat capacity and structural factors such as Lindemann index. In addition to this geometries of different local minima visited during the MC simulation will be presented.

[1]. R. Iftimie, D. Salahub, D. Wei, and J. Schofield, *J. Chem. Phys.* 113, 4852 (2000).

[2]. R. Fournier, M. Zhang, Y. Soudagar, and M. Hopkinson, *Lecture Series on Computers and Computational Sciences*; T. E. Simos, G. Maroulis, Eds. VSP Brill Academic Publishers: Utrecht, The Netherlands, 3, 51 (2005).

Conformational Behavior of Chemisorbed Azobenzene Derivatives in External Electric Fields: A Theoretical Study

Chris Chapman and Irina Paci

Department of Chemistry, University of Victoria, PO Box 3065, Victoria, BC, V8W 3V6

Azobenzene derivatives have been shown to act as molecular switches when exposed to an applied electric field or tunneling electrons. Many applications require the switching molecule to be adsorbed on a surface. However, stable conformations and the isomerization energetics of adsorbed azobenzenes can be very different from the analogous more thoroughly studied behaviors in gas phase or liquid solution. In this study, we investigate the zero-density limit behavior of cis and trans N-(2-mercaptoethyl)-4-phenylazobenzamide chemisorbed on a Au(111) surface. For all calculations, we employ the Perdew-Burke-Erzenhof functional as implemented in the SIESTA package, with a double-zeta plus polarization basis set. A large number of starting geometries were equilibrated and several stable configurations were identified for both the trans- and cis-adsorbed isomers. The most stable are those in which the azobenzene moiety is parallel to the surface. Applied external electric fields in the usual STM range of $\pm 1 - 3$ V/nm produce minimal changes in these geometries. We find that the strength of the dispersive interactions between the extended

conjugated system and the metallic surface is such that switching between parallel and upright geometries of single-molecules is unlikely to occur because of coupling to such a field. Although the presence of the surface slightly modifies the ground electronic state pathways for isomerization, this process is also not accessible through simple field-molecule coupling effects.

Implementation of Quantum Gate Operations with Vibronic States Manipulated by Stark-Chirped Rapid Adiabatic Passage

Hyeonho Choi^{1,2}, Yukiyoishi Ohtsuki² and Seokmin Shin¹

¹Department of Chemistry, Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul 151-747, Republic of Korea

²Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aramaki Aza Aoba, Aoba-ku, Sendai 980-8578, Japan

In some of the theoretical studies, optimal control theory (OCT) is adopted to design gate pulses with the aim of numerically demonstrating the usefulness of molecular qubits. These optimal gate pulses utilize non-adiabatic optical transition. On the other hand, adiabatic passage (AP) techniques can be also used to control quantum systems. They are originally proposed to control population transfer and are known to be robust against pulse areas and shapes as long as the adiabatic condition is satisfied.

The purpose of the present study is to propose a SCRAP-based scheme, which can be an alternative to a STIRAP-based scheme, to manipulate molecular qubits. One of the characteristics of SCRAP is to actively use laser-induced Stark shift as control knobs. If we use a resonant pump pulse and a far off-resonant Stark pulse in SCRAP, we can introduce half-SCRAP that is one of the variations of SCRAP and is originally used to create coherent superpositions. Taking vibronic states of NO as molecular qubit, we apply half-SCRAP to the gate operation on one-qubit molecular system and extend it to two-qubit molecular system designing the CNOT gate.

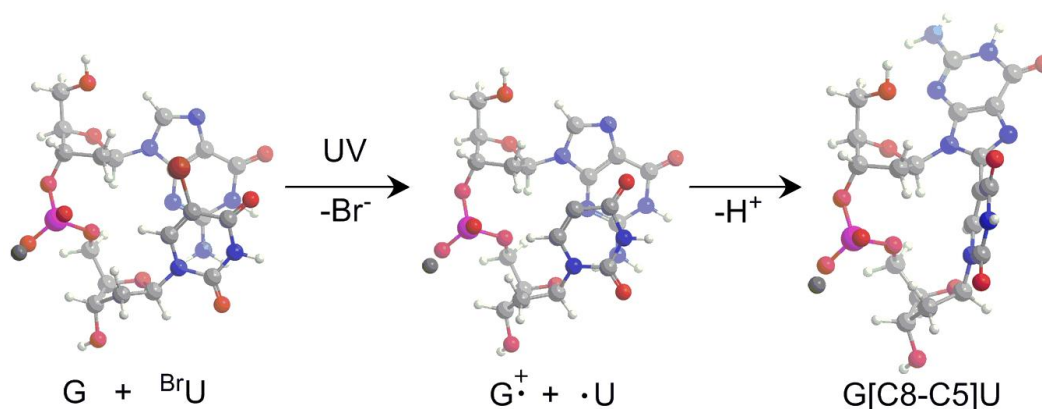
The Formation of a DNA Intrastrand Cross-link Between Guanine and the Uracil-5-yl Radical

Cassandra D.M. Churchill and Stacey D. Wetmore

Department of Chemistry and Biochemistry, University of Lethbridge, 4401 University Drive, Lethbridge, Alberta, T1K 3M4

Incorporation of the anti-tumour agent, 5-bromouracil, into DNA, followed by UV or γ irradiation generates the uracil-5-yl radical. This radical subsequently reacts to form a variety of DNA-damaging products, including intrastrand cross-links, which may induce tumour cell death. While experimental work has identified four major intrastrand cross-link products following UV-irradiation of 5-bromouracil-containing DNA, the exact structures and reaction mechanisms for cross-link formation are unknown. The present poster begins to address these deficiencies with an in-depth study of the experimentally-predicted most abundant intrastrand cross-link, which occurs between the C8 site of 5'-guanine and the C5 site of the 3'-uracil radical (5'-G[C8-C5]U-3').

In our study, extensive testing first identified the most accurate and efficient computational model to be the dinucleoside monophosphate, which includes a Na^+ counterion for charge neutralization, used in conjunction with the M06-2X functional and implicit solvent effects. Using this combination, the reactant and product structures are analyzed and compared to natural duplex DNA. The structure of the 5'-G[C8-C5]U-3' intrastrand cross-link reveals a change in the base-base orientation, indicative of its potential to distort the DNA double helix. Subsequently, both UV and γ pathways for the formation of the 5'-G[C8-C5]U-3' cross-link are considered. Significant differences are found between the two pathways. Most notably, cross-link formation along the UV pathway proceeds via an intersystem crossing (ISC), while the analogous step in the γ pathway involves a true transition state. This work provides a basis for the study of the remaining experimentally-observed intrastrand cross-links. Combined, this work will contribute to an ultimate understanding of cross-link formation, as well as provide a measure of the DNA-damaging capabilities of the uracil radical.



MMH-2 as a New Approach for the Prediction of Intermolecular Interactions: The Crystal Packing of Acetamide

Edelsys Codorniu-Hernandez¹, A. Daniel Boese², Carsten Schauerte², Alberto Rolo-Naranjo³, Luis Alberto Montero-Cabrera⁴ and Roland Boese²

¹Department of Chemistry. University of Calgary. 2500 University Drive, NW. Calgary. Canada

²Department of Chemistry. University of Duisburg-Essen. Essen, Germany

³Institute of Technologies and Applied Sciences. Havana, Cuba

⁴Laboratory of Computational and Theoretical Chemistry. University of Havana, Cuba

A new approach (MMH-2) was applied and tested for the prediction of intermolecular interactions in the crystal packing of acetamide. In MMH-2, energies of random molecular interaction configurations are computed. It uses molecular association quantities from statistical thermodynamics in order to obtain intermolecular interaction motifs that follow a ranking process. The most important motifs are optimized. Here, the AM1 semiempirical Hamiltonian was applied for the calculation and optimization of each obtained configuration and a comparison to MP2 results is provided. Such a stepwise procedure follows the assumed genesis of crystal growth without using experimental input. For evaluation purposes, graph set analysis was used to classify the structural patterns of both acetamide polymorphs. It was also necessary to introduce a new geometrical similarity index for the comparison of calculated and experimental motifs. As a result, all experimental hydrogen bond patterns were found and molecular synthons in both polymorphic acetamide structures were predicted as local minima. This suggests a new strategy for crystal structure prediction of flexible molecules with a possible subsequent progress in crystal engineering in silico.

Codorniu-Hernandez E., Boese A-D. , Carsten Schauerte, Rolo-Naranjo A., Miranda-Quintana R., Montero-Cabrera L-A., Boese R., CrystEngComm, 2009, 11, 2358-2370.

MCTDH Quantum Dynamics Using Potential Energy Surfaces Fitted by Neural Networks: A Benchmark Study

Javier E. Cuervo¹ and Alex Brown²

¹Institute for Biocomplexity and Informatics, University of Calgary, 2500 University Dr. N.W. Calgary, Alberta, Canada T2N 1N4

²Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive, Edmonton, Alberta T6G 2G2

In this work, we use neural networks (NN) to fit molecular potential energy surfaces (PES) to an analytic function. In particular, we are interested in potential energy functions (PEF) that have the form of a sum of products of single-coordinate functions. This functional form is desirable for computational efficiency in the context of quantum dynamics calculations using the multiconfiguration time-dependent Hartree method (MCTDH). It has been shown that NNs with exponential transfer functions can accurately reproduce PESs using fewer fitting terms than current comparable methodologies. Herein, two different systems, ammonia (NH_3) and formyl fluoride (HFCO), are used to test this methodology. The ultimate goal of this research is to obtain compact PEFs that will allow the efficient implementation of optimal control theory within the MCTDH framework.

Utilizing Configurational Thermostats in MD Simulations of Homogeneous Nucleation

Harro Dittmar, David Knippers and Peter Kusalik

Department of Chemistry, University of Calgary, Alberta, Canada

The homogeneous nucleation of liquid systems is an activated non-equilibrium process that typically is too unlikely to be observed in standard MD simulations. In previous studies of our research group it was demonstrated that simultaneous application of two counteracting thermostating mechanisms can significantly increase the number of nucleation events in deeply supercooled Lennard Jones (LJ) fluids and a model of liquid CO₂. In this setup one thermostat controls the kinetic and the other one controls the configurational temperature, maintaining a higher value of the latter. Ultimately this technique might provide an approach to homogeneous nucleation that is less biased than driving the crystal formation by non-Boltzmann sampling or path sampling with the aid of structural order parameters.

Since the derivation of the configurational temperature used in the thermostat is based on the equilibrium entropy, its meaning for non-equilibrium processes is still unclear. My current work is aimed at clarifying which aspects of homogeneous nucleation are correctly described by this setup and to define the differences between completely free nucleation and a nucleation driven by the non-equilibrium temperature gradient. We plan to analyze the flow of entropy due to each thermostat for nucleation events in the LJ fluid. The flow of entropy in and out of the system will be checked against an approximate entropy change calculated from the radial distribution functions (according to Chakravarty et al.). We expect the results to provide insight in how to design efficient entropy lowering thermostating schemes for molecular systems like liquid CO₂ and H₂O.

Email: h.dittmar@ucalgary.ca, d.knippers@ucalgary.ca, pkusalik@ucalgary.ca

Microscopic Solvation and Thermodynamics of Prion Protein Structural Transformations Induced by High Temperature

Lyudmyla Dorosh^{1,2}, *Nikolay Blinov*^{1,2}, *Mark Berjanskii*^{1,3}, *David Wishart*^{1,3} and *Andriy Kovalenko*^{1,2}

¹National Institute for Nanotechnology, NRC, Edmonton, AB, Canada T6G 2M9;
Andriy.Kovalenko@nrc-cnrc.gc.ca

²Department of Mechanical Engineering, University of Alberta, Edmonton, AB, Canada T6G 2G8; Dorosh@ualberta.ca

³Department of Biological Sciences, University of Alberta, Edmonton, AB, Canada T6G 2E9

The misfolded prion protein is necessary for the development of transmissible spongiform encephalopathies in mammal. According to the protein only hypothesis the conformational conversion from soluble cellular prion PrP^C to the oligomeric scrapie isoform PrP^{SC}, can activate the formation of toxic amyloid fibril, which disrupt the normal tissue structure. The molecular details of such conversion and 3D structure of PrP^{SC} remain poorly understood because of insolubility of PrP^{SC}. In this work we have used the approach which combines molecular dynamics (MD), molecular mechanics and the three-dimensional molecular theory of solvation (3D-RISM-KH)[1] to provide insight into thermodynamics of structural transitions of human prion protein (huPrP)[2].

The high temperature MD simulations demonstrate the tendency for unfolding in the C-terminal parts of helices H2 and H3. Their core remains relatively stable, supported by the disulphide bond. Helix H1 detaches from the H2-H3 bundle [3]. In agreement with the previous experimental and theoretical results [2-4] our data shows that the stability of helix H1 and the elongation of β -strands S1 and S2 are affected by several intra-helix salt bridges involving D144, R148, R151, E152 and intra-protein bridges involving R156, R164. The salt bridges involving K204 and R208 stabilize helix H3.

Here we show that the exposure of charged and polar residues to the solvent strongly affects the free energy for the first 4 ns. At this stage of unfolding, when the secondary structure of the protein begins to disrupt, solvation electrostatic interactions were found as a strongest factor opposing unfolding. The next 6 ns of unfolding is characterized by the domination of the non-electrostatic effects, mainly the van der Waals intra-protein interactions, non-electrostatic protein-solvent interactions, and non-electrostatic solvation entropy.

A strong anti-correlation of the free energy of unfolding with α -helical content, and, correspondingly, decrease of the solvent accessible surface areas (ASA) of charged and polar residues upon unfolding were found. At the same time, the ASA of the non-polar residues increases upon unfolding (as well as the total ASA), with implication for the non-electrostatic solvation entropy and structural stability of huPrP. The analysis of the free energy of unfolding resolved on per residue basis reveals that R156, R208, R136, D167A, and Y128 residues essentially contribute to the unfolding energy by reforming salt bridges/hydrogen bonds.

[1] A. Kovalenko in: *Molecular Theory of Solvation*, Fumio Hirata (Ed.), Kluwer Academic Publishers, Dordrecht, 2003, pp.169-275.

[2] R. Zahn et al., *PNAS* **97** (11),145-150 (2000).

[3] M.L. DeMarco and V. Daggett, *Biochemistry* **46**: 3045-3054 (2007).

[4] W. Guest et al, *Biochem. Cell Biol.* **88**, 371-381 (2010).

A17

Energies from Model Kohn-Sham Potentials: Aufbau and Janak Paths

Pavel D. Elkind and Viktor N. Staroverov

Department of Chemistry, The University of Western Ontario, London, Ontario N6A 5B7,
Canada

The Levy-Perdew virial relation is just one way of assigning an energy to a model exchange potential. We investigate two alternative energy expressions that are based on the van Leeuwen-Baerends line integral formula and involve two new density transformation paths. In the first scheme, the potential is integrated along a path of densities constructed by filling frozen orbitals in accordance with the aufbau principle. In the second scheme, referred to as the Janak path, the energy is obtained by integrating the HOMO energy over fractional HOMO occupation numbers. Energies obtained from model potentials in this manner are close to the values obtained by the so-called density scaling path, but deviate significantly from the values yielded by the Levy-Perdew virial relation.

A18

Simple Orbital Theory of Molecular Conductors

Matthias Ernzerhof

Department of Chemistry, University of Montréal, e-mail:
Matthias.Ernzerhof@UMontreal.ca

Ballistic electron transport through molecules occurs, for instance, in STM imaging and in conductance measurements of molecular electronic devices. In these experiments, molecules are connected to macroscopic contacts and the electron current through the molecules is measured. Recently [1], a number of basic interference phenomena have been identified that facilitate the interpretation of STM images and molecular transmission probabilities. In the present work, we present a molecular-orbital-type theory [2] that provides simple rules for the analysis of these phenomena. We illustrate our approach by showing how side groups, attached to molecular wires, can completely suppress the conductance. Furthermore, we discuss interference effects in aromatic molecules which also inhibit electron transport.

[1] G.C. Solomon, C. Herrmann, T. Hansen, V. Mujica, M.A. Ratner, *Nature Chemistry* 2, 223 (2010); P. Rocheleau, M. Ernzerhof, *JCP*, 130, 184704 (2009); G.C. Solomon, D.Q. Andrews, T. Hansen, R.H. Goldsmith, M.R. Wasielewski, R. P. Van Duyne, M.A. Ratner, *JCP*, 129, 054701 (2008); M. Ernzerhof, H. Bahmann, F. Goyer, M. Zhuang, P. Rocheleau, *JCTC*, 2, 1291 (2006); M. Ernzerhof, M. Zhuang, P. Rocheleau, *JCP*, 123, 134704 (2005).

[2] M. Ernzerhof, F. Goyer, *JCTC*, 6, 1818 (2010); M. Ernzerhof, in preparation.

A19

Coarse-Grained Modelling of Gas-Phase Protein Complexes

Sarah K. Fegan and Mark Thachuk

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, V6T 1Z1, Canada

We are interested in studying the gas-phase dissociation of protein complexes in order to better understand how the dissociation patterns in mass spectra relate to the structure of the protein complexes. Previous work in our group used an all-atom force-field to model the dissociation of a dimer with fixed positive charges. These studies suggested that dissociation of the dimer into two monomers with the same charge (symmetric dissociation) would be favoured. However, asymmetric dissociation has been observed in experiments (for example see the work of Jurchen and Williams, *J. Am. Chem. Soc.* **125**, 2817-2826 (2003)).

Coarse-grained models represent groups of atoms as a single bead, thus using fewer particles to represent a given system allowing for faster molecular dynamics simulations. Once we validate a coarse-grained force-field for the gas-phase protein complex system, we plan to include the effects of allowing charges to move. Preliminary results will be shown.

A20

MCP and All-Electron Studies of HRgF Molecules

*Amelia Fitzsimmons*¹, *Mariusz Klobukowski*¹, *Hirotohi Mori*² and *Eisaku Miyoshi*³

¹Department of Chemistry, University of Alberta, Edmonton, AB T6G 2G2, Canada

²Division of Advanced Sciences, Ocha-dai Academic Production, Ochanomizu University, 2-1-1 Ohtsuka, Bunkyo-ku, Tokyo, 112-8610, Japan

³Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga Park, Fukuoka 816-8580, Japan

Molecules HRgF, where Rg= Ar, Kr, Xe, Rn were studied at levels of theory that included electron correlation, taking relativistic effects into account by either using the recently developed parametrization of the extended model core potentials and basis sets or by using the Douglas-Kroll method with all-electron basis sets. Charge distributions were calculated according to Mulliken, Lowdin, and natural bond orbital methods of population analysis and the results of these methods were compared, confirming that bonding in these molecules corresponds to the interaction between the fluoride anion and the RgH⁺ moiety. In contrast to previously reported results, the present calculations show that HRnF is more stable than compounds of the lighter congeners. Trends in first ionization energies, bond lengths, and energies of formation and decomposition are discussed and found to be consistent with the periodic trends of the atomic properties of rare gases.

Potential Energy Surface Exploration with Particle Swarms*Rene Fournier and Satya Bulusu*

Department of Chemistry, York University, Toronto, ON, Canada M3J 1P3

We are interested in the following computational problem. Starting from a molecular structure, usually at or near a local minimum of the PES, follow a low energy path to a critical point and keep walking through a series of critical points without ever visiting the same point twice. This would, in principle, produce a sequence M1–S12–M2–S23–M3... of minima and saddle points akin to a reaction mechanism. We developed an evolutionary algorithm similar to a Particle Swarm Optimization (PSO) to solve this problem.

In a typical run, between 4 and 8 randomly distorted versions of the initial geometry are created: they are “particles” and collectively make up a “swarm”. At each iteration, we evolve particles by taking steps of fixed size “s”. A step is “good” if it moves away from previously visited geometries and produces a decrease, or small increase, in energy. In analogy to PSO, we assign fitness to particles, and let every particle move toward the current best.

The sequence of geometries, energies, and gradients can be analyzed to identify crossings from one valley to another. This gives us estimates of structures and energies of minima and transition states. I will show results of sample runs on small systems like HCN, 1,2-difluoroethylene, and cyclopropane that display isomerization.

A22

Identification of γ -tubulin Paclitaxel and Colchicine Binding Locations for Novel Dual Inhibitors of γ and β III-tubulin

Douglas Friesen¹, Khaled Barakat², Bruce Fenske¹, Jonathan Mane¹, Chih-Yuan Tseng¹ and Jack Tuszynski^{1,2}

¹Dept. of Oncology, Cross Cancer Institute, Edmonton, AB, T6G 1Z2

²Dept. of Physics, University of Alberta, Edmonton, AB, T6G 2G7

Recent studies have shown an overexpression of γ -tubulin and β III-tubulin in human glioblastomas and glioblastoma cell lines. As the two-year survival rate for glioblastoma is still very poor, there is a great potential benefit for discovering novel chemotherapeutic agents that can act as dual-inhibitors of γ -tubulin and β III-tubulin. γ -Tubulin is known to form a ring complex which acts as a foundation for microtubule nucleation. Its tertiary structure is quite similar to curved β -tubulin. As no γ -tubulin small molecular inhibitors are known to exist, we have performed molecular dynamics (MD) simulations to analyze the homologous γ -tubulin binding domains of paclitaxel and colchicine, two drugs whose binding sites to β -tubulin are well characterized through crystallography. MD characterization of these promising binding sites on γ -tubulin can lead to our subsequent rational design of novel inhibitors of γ -tubulin.

A23

Analytic Integrability Conditions for Model Kohn-Sham Potentials

Alex P. Gaiduk and Viktor N. Staroverov

Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7,
Canada

In order for a model Kohn-Sham potential to yield meaningful physical properties, it must be a functional derivative of some density functional, that is, be integrable. We present practical integrability conditions for explicitly density-dependent potentials which can be readily used to identify model potentials that have no parent functionals and to turn such potentials into functional derivatives. We illustrate application of our technique by transforming the popular model potential of van Leeuwen and Baerends into a functional derivative.

Laulimalide, Peloruside and Their Derivatives: Study Towards An Understanding of Their Anti-Mitotic Behavior

Melissa Gajewski^{1,2}, *Mariusz Klobukowski*¹ and *Jack Tuszynski*²

¹Dept. of Chemistry, University of Alberta, Edmonton, AB, T6G 2G2

²Dept. of Oncology, Cross Cancer Institute, Edmonton, AB, T6G 1Z2

Due to the involvement of microtubules in cell division, they are an important focus of studies of dividing cells, in particular in the area of anti-cancer research. Some drugs currently used in chemotherapy work by interfering with cellular division through binding to the α,β -tubulin heterodimer. There are eight common isotypes of β tubulin that are present in varying degrees in the human body; all of these isotypes have known mutations some of which correlate with known drug resistance to standard chemotherapy. Peloruside and laulimalide are potential candidate drugs for improved cancer chemotherapy.

These drugs show promise for future clinical use, but both present some unique problems in their parent form. Molecular Dynamic (MD) calculations were done on eleven isotypes of tubulin (1TUB, β I, β IIa, β IIb, β III, β IVa, β IVb, β V, β VI, β VII, and β VIII) with peloruside A & B, laulimalide and both known derivatives and some de novo designed derivatives. The ΔG values are calculated for all 53 compounds (25 peloruside based derivatives & 28 laulimalide based derivatives) with each of the eleven isotypes of tubulin. These drugs show different selectivity to the tubulin isotypes and this property can be manipulated in order to selectively kill cancerous cells with an overproduction on one or more of tubulin isotypes.

AM1 semi-empirical calculations on the ligands (peloruside, laulimalide and their derivatives) were performed, as well as Molecular Dynamics (MD) simulations using the Amber force field and Molecular Mechanics (MM) approach. MM studies were performed on ligand and tubulin protein. The interactions of the ligand and protein were studied and the binding affinities of the interaction of ligand and protein will be analyzed. In this work we report our preliminary results of these studies.

Molecular engineering of cancer drugs could lead to a derivative that works synergistically with other cancer drugs to eradicate all of the cancer cells. A matrix of binding affinities of different tubulin isotypes to derivatives of the ligands will eventually be created in order to find derivatives that increase specific binding to the α, β -tubulin heterodimer.

Experimental and Theoretical Studies on the 2,6-dimethoxy para-benzoquinone Anion Radical: An Approach to the Correct Estimation of Isotropic Hyperfine Couplings

Haleh Hashemi Haeri, Reinhard Kappl and Markus Hoth

Fachrichtung 2.5 Biophysik, Universitt des Saarlandes, Klinikum, Geb. 76, 66421
Homburg/Saar, Germany hashemihaeri@gmail.com

It is well established that in the presence of hydroxide ion (OH^-), quinones are forming a radical species, known as semiquinones. These para-benzoquinone radical anions are considered as model systems for the semiquinone radicals derived from the important class of ubiquinone molecules in the electron transport chain of mitochondrial membranes. The structure of 2,6-dimethoxy para-benzoquinone (2,6-PBQ) radical anion in alkaline medium was investigated both experimentally and theoretically by EPR spectroscopy and DFT methods, respectively. X-band EPR spectra were measured on a Bruker spectrometer. Quantitative EPR evaluation shows that this radical, at its peak concentration, amounts to about 4% of the used total 2,6-PBQ concentration. The spectral simulations yield the hyperfine interactions and allow to conclude on the radical structure.

All the theoretical calculations for the semiquinone radical of 2,6-PBQ were performed with the Gaussian03 software package. As outlined in several papers the B3LYP method is one of the most efficient methods for calculation of hyperfine constants. This method together with EPR-III and 6-311+G** basis sets were used in this study. To obtain the theoretical hyperfine couplings, the structure was treated in different media of gas and solution considering water as the main solvent. In the case of water solvent both implicit and explicit behaviors were tested. It was found that the polarization effect due to change in environment and the site specificity of the molecule plays an important role on the correct estimation of the hyperfine coupling values. Also a direct relationship can be seen between the hyperfine values and the direction of the water molecule dihedral angle toward the structure. The information on the Singly Occupied Molecular Orbital (SOMO) shows that the unpaired electron changes its location when the media properties are altered. The best consistency between the experimental and theoretical values is obtained by introducing explicit water molecules to the structure. Different sites of the water molecule were considered with respect to the 2,6-PBQ radical structure to approach the experimental values of interacting protons more closely.

Light Induced Oxidation Sensitized by Flavins: A Theoretical Approach*Paula Homem-de-Mello¹ and Daniel R. Cardoso²*¹ABCSim, Universidade Federal do ABC, Santo André/SP - Brasil²IQSC, Universidade de São Paulo, São Carlos/SP - Brasil

Riboflavin (RF) and its derivatives, generally referred as vitamin B2, are among the most important photosensitizers in biological and food systems. For example, milk and dairy products are important sources of riboflavin, and the high content of this vitamin makes light-induced oxidation sensitized by riboflavin the major factor promoting oxidation during storage, causing nutritional losses and yielding undesirable flavors and toxic compounds. [1,2] The triplet excited state of riboflavin is a strong electron acceptor and has a oxidation potential of 1.7 V vs. NHE. In this way, compounds that are easily oxidized therefore react via electron transfer or hydrogen atom transfer with 3Rib^* forming a riboflavin radical and an oxidized substrate radical cation which most probably will be highly reactive and therefore quickly undergo subsequent reactions. Deactivation of triplet states by electron transfer or hydrogen atom transfer is called Type I photooxidation mechanism or it may be deactivated by energy transfer to molecular dioxygen yielding singlet excited oxygen as the reactive intermediate (Type II). Since reactive triplet excited riboflavin is considered to be a pivotal intermediate in both Type I and Type II photooxidation reactions, a insight study in the quenching mechanism was the aim of this work. Thus, we have performed DFT calculations with focus on flavin derivatives as photosensitizers to investigate the reactivity of singlet and triplet-excited states toward purine bases and model lipid systems (i.e., methyl esters of fatty acids). These results were useful to determine the photooxidation mechanism (Type I or Type II) for each system as well a insight into the Type I mechanism (electron-transfer or hydrogen atom transfer). The inclusion of solvation effects was fundamental to obtain a good correlation with experimental data. [3,4]Details of calculation: all structures were optimized with the B3LYP functional. The absence of imaginary frequencies was used as a criterion to ensure that the optimized structures represent the minimum of the potential energy surface. Bond dissociation energy (BDE) was calculated by use of the expressions presented by DiLabio et al. [5] The lowest triplet excitation energies (ET1) of riboflavin and unsaturated fatty acids methyl ester were estimated by TD-DFT. Vertical electron affinities (VEA), hydrogen atom affinity (HAA), and vertical ionization potentials (VIP) of riboflavin, purine bases and unsaturated fatty acids were also calculated. Acetonitrile and ethanol solution was simulated with Integral Equation Formalism as Polarizable Continuum Model (IEF-PCM).

Acknowledgments: Brazilian agencies FAPESP and CNPq.

- [1] Cardoso, D.R. et al. *J. Agric. Food Chem.* 2004, 52, 6602-6606.
- [2] Bradley, R.L.J. *J. Food Prot.* 1980, 43, 314-320.
- [3] Cardoso, D.R. et al. *J. Agric. Food Chem.* 2005, 53, 3679-3684.
- [4] Huvaere, K. et al. *J. Phys. Chem. B* 2010, 114, 55835593.
- [5] DiLabio, G. A. et al. *J. Phys. Chem. A* 1999, 103, 16531661.

Survival of the Fittest Oxide: Tuning Ionic and Electronic Properties of Doped Metal Oxides by Genetic Algorithm Optimization

James Hooper and Tom K. Woo

Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa, ON, Canada
K1N 6N5

Doped metal oxides have many applications as substrates in catalysis, as gas sensors, and as next generation solid electrolytes in solid-oxide fuel cell technologies, just to name a few. The performance of these metal oxide materials can be attenuated via doping of the parent oxide with other elements at varying concentrations. However, the optimization of the composition is often performed by trial and error. We have developed a genetic algorithm based approach to both find the lowest energy configuration of a specific metal oxide composition and to search the chemical space to optimize a specific property of interest based on a given metric evaluated at the DFT level of theory. Specifically, this approach is demonstrated by optimizing electronic mobility in doped zinc and tin metal oxides, which are used in gas sensor technologies. The approach is also used to study Lanthanide doped ceria (LDC) which is used as a solid electrolyte in solid-oxide fuel cells. The nature of defect associations in LDC materials ($L = Y, La, Nd, Sm, Gd, Er, Yb, \text{ and } Lu$) are then used in a “proof of principle” context to extract optimal ionic conductivities with regards to both the dopant atom’s identity and its concentration.

pCCSD: Parameterized Coupled-Cluster Theory with Single and Double Excitations

Lee M.J. Huntington and Marcel Nooijen

Department of Chemistry, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, Canada, N2L 3G1

The major characteristics of traditional single reference coupled cluster (CC) theory are size-extensivity, invariance under orbital rotations of the occupied and virtual space, and exactness for 2 electron systems in the case of CCSD, 3 electrons for CCSDT and so forth. One may ask whether or not CC theory is the only theory which displays these desirable properties, and moreover if it is not, if the traditional CC approach is actually the best choice.

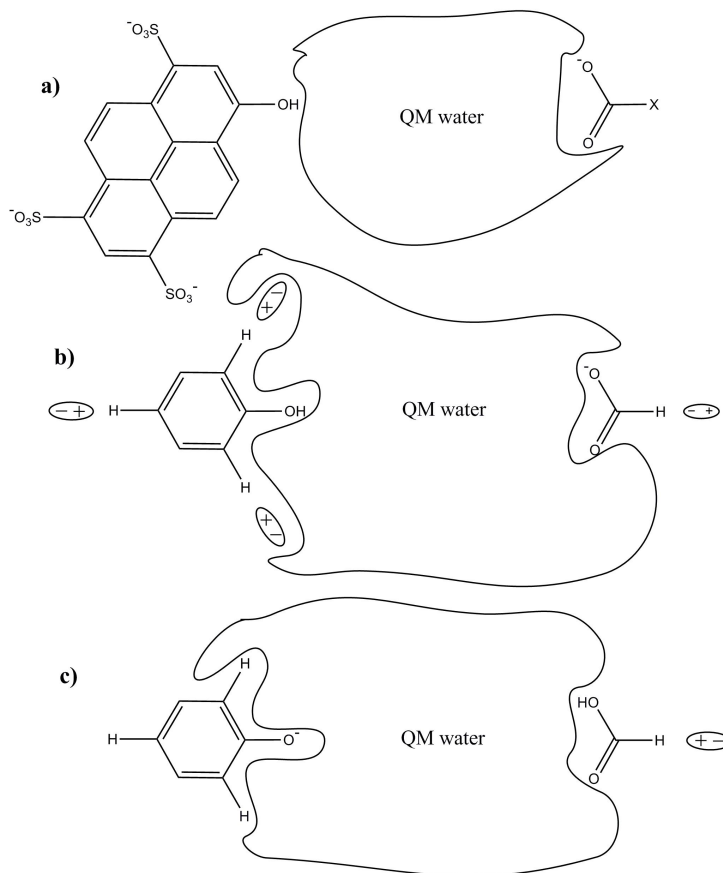
In this work, we propose a continuous class of methodologies that are related to CCSD and are inspired by the coupled electron pair approximations (CEPA). It will be shown that one can systematically improve upon CCSD and obtain geometries, vibrational frequencies, and total energies from a parameterized version of CC theory (picking a particular member from a continuous family of approaches) that often approaches the accuracy of CCSD(T). Also, for single bond breaking phenomena the parameterized methodology is surprisingly accurate. The method has been implemented in ACES2 and more recently, a localized pair natural orbital (LPNO) version of the methodology has been implemented in the ORCA software package, developed in Frank Neese's group at the University of Bonn. The LPNO based methodology allows routine (black-box) applications to intermediate sized (50-100 atoms) molecular systems.

A Computational Model for the Study of Ultrafast Acid-Base Neutralization Reactions

Radu Iftimie, Patrick Maurer and Vibin Thomas

Department of Chemistry, University of Montréal

Ultrafast, time-resolved investigations of acid-base neutralization reactions have recently been performed using photoacids containing 8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS) and various Brønsted bases. Two conflicting neutralization mechanisms have been formulated by Mohammed et al, *Science* 2005, **310**, 83 and Siwick et al, *J. Am. Chem. Soc.* 2007, **129**, 13412 for the same acid-base system. Herein we formulate an ab initio molecular dynamics based computational model which is able to investigate the validity of the proposed mechanisms in the general context of ground-state acid-base neutralization reactions. The present approach employs 2,4,6 tricyanophenol (exp. pKa 1) as a model for excited-state HPTS* (pKa 1.4) and carboxylate ions for the accepting base, in conjunction with our recently-proposed dipole-field/QM treatment (Maurer et al, *J. Chem. Phys.* 2010, **132**, 074112) of the proton donor and acceptor molecules, which allows us to tune the free energy of the neutralization reaction to any desired value. We demonstrate that the dipole-field/QM model reproduces correctly key properties of the tricyanophenol acid molecule including gas-phase proton dissociation energies and dipole moments, and condensed-phase hydration structure and pKa values.



Implementation of Feynman Path Integral Methods in the Molecular Modelling Toolkit

Christopher Ing¹, Konrad Hinsen³ and Pierre-Nicholas Roy²

¹Department of Physics, University of Waterloo, 200 University Avenue West Waterloo, Ontario, Canada N2L 3G1

²Department of Chemistry, University of Waterloo, 200 University Avenue West Waterloo, Ontario, Canada N2L 3G1

³Centre de Biophysique Moléculaire, CNRS Orléans Synchrotron Soleil - Division Expériences, Saint Aubin - BP 48 91192 Gif sur Yvette Cedex, France

We present an implementation of path integral molecular dynamics in the Molecular Modeling Toolkit (MMTK) software package and its applications to model systems and He-CO₂ clusters. We address the optimization of the Langevin friction parameter and present a bead convergence study in order to optimize computational performance while correctly matching structural and energetic properties of high-accuracy path integral Monte Carlo data. Furthermore, we present a variation on this implementation used to estimate ground state observables using path integral ground state molecular dynamics in MMTK.

Theoretical Study on the Geometric and Electronic Structures, and the Anion Photoelectron Spectra (PES) of the LiAl_n^- ($n=3-13$) Clusters

*Chiaki Ishibashi*¹ and *Hidenori Matsuzawa*^{1,2}

¹Department of Life and Environmental Sciences, Chiba Institute of Technology, 2-17-1 Tsudanuma, Narashino, Chiba 275-0016, JAPAN

²Department of Chemistry, Center of Education, Chiba Institute of Technology, 2-1-1 Shibazono, Narashino, Chiba 275-0023, JAPAN

The photoelectron spectra of the LiAl_n^- ($n = 3 - 13$) clusters were measured by O. C. Thomas *et al.*[1] The peak shape of the anion PES changes from $n = 8$ to 9 and $n = 12$ to 13. It is expected that the geometric and electronic structures are closely related to the shape of the anion PES. The aim of this study is to investigate the relationship between the geometric and electronic structures and the peak shape of the anion PES. The stable structures were examined by using the B3LYP method with the 6-311+G* basis set. The VDE values were obtained with the TD-DFT calculation.

In the LiAl_n^- ($n = 3 - 13$) clusters, the calculated VDE values at the stable structures are in good agreement with the anion PES data. The anion PES with the results of the VDE and the stable structure, of $n = 8$ and 9, were shown in Fig.1. The stable structure for $n = 8$ has the octahedral skeleton without the central Al atom. On the other hand, that for $n = 9$ is wheel-like type with the central Al atoms. Both two large peaks in the LiAl_8^- cluster were assigned to the detachment of the β -electron. The large peak was also assigned to that of the β -electron though the small peak corresponds to that of the α -electron in the LiAl_9^- cluster. A large peak of $n = 9$ includes the binding energies of 12a and 13a corresponding to 4a'' and 9a' of $n = 8$. It is assumed that the peak shape changes from $n = 8$ to 9 are related to the geometric pattern change.

The relationship between the anion PES and the geometric and electronic structures of the Li-Al clusters was discussed on the basis of the molecular orbital theory and the shell model. The hybridization of 3s (Al) and 3p (Al) atomic orbital does not occur in the occupied molecular orbital of the LiAl_8^- cluster. In the LiAl_9^- cluster, 3s orbital component hybridizes to some occupied molecular orbital including the 3p orbital component. The 3s – 3p hybridization occurs in $n > 8$. The central Al atoms play an important role for the formation of the 3s – 3p hybridization.

By the way, the peaks of the anion PES for $n = 12$ and 13 of the LiAl_n^- cluster are noticed. The small peak at 2.0eV appears in the PES for $n = 13$. No change of the geometric and shell structures is found. Therefore, it is suggested that the peak change between $n = 12$ and 13 is different from that between $n = 8$ and 9. The electron detachment from the 1g shell corresponds to the small peak.

We conclude that the sudden change of the peak shape in the anion PES is related to the change of geometric and electronic structures in the LiAl_n^- ($n = 3 - 13$) clusters.

[1] O. C. Thomas, *et al.*, *J. Chem. Phys.*, **114**, 9895 (2001)

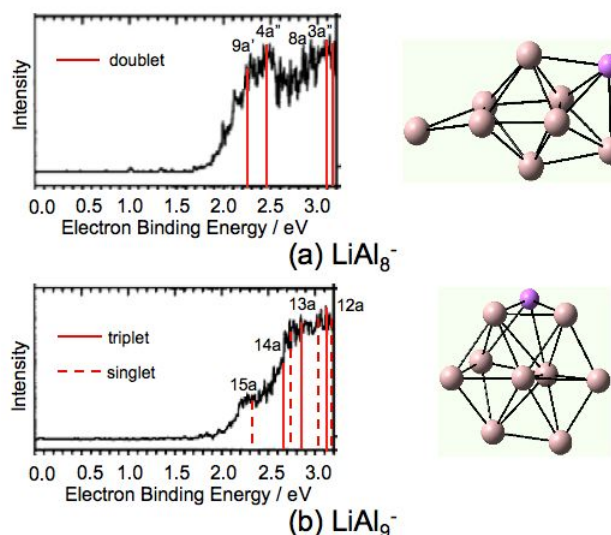


Fig. 1 Anion PES with the VDE sticks and stable structure of LiAl_8^- (a) and LiAl_9^- (b).

Simulation Studies of Biologically Relevant Oligo-arabinofuranosides*Shahid Islam*¹, *Todd Lowary*² and *Pierre-Nicholas Roy*¹¹Department of Chemistry, University of Waterloo, Waterloo, ON, N2L 3G1, Canada²Carbohydrate Science, Department of Chemistry, University of Alberta, Edmonton, AB, Canada T6G 2G2

Furanoside containing polysaccharides are biosynthesized by a number of organisms such as bacteria, fungi, and parasites. It is suggested that these furanosides play an important role in the survival and pathogenicity of different diseases in the human body such as Tuberculosis, *C. difficile* and leprosy. Furanosyl moieties are highly flexible compared to their pyranoside counterpart. A deeper understanding of the conformational and binding preferences of furanosyl molecules is therefore very important.

Simulations of a series of mono and oligo- arabinofuranosides were carried out with long molecular dynamics (MD) and umbrella sampling simulations using the AMBER force field and the GLYCAM carbohydrate parameter set. The rotamer population distribution about the exocyclic C – C bonds and the puckering distributions of the rings obtained from umbrella sampling simulations were found in excellent agreement with those obtained from long MD simulations for small monosaccharide fragments. We calculate ensemble average vicinal proton-proton coupling constants based on available Karplus-like relationships, and compare our results to experimental measurements. For oligo arabinofuranosides, rotamer population about the linked C – C bonds did not follow the same trend with experiments. To understand this disagreement, we have performed semi empirical calculations of mono and di-arabinofuranosides on the fly. Our initial study showed interesting results.

We also studied the conformational changes to $\alpha - (1 \rightarrow 5)$ -linked L-arabinohexaose (Ligand) upon binding to arabinanase (protein) in solution. We carried out potential of mean force calculations to predict binding free energy of the ligand and protein. Our theoretical results will provide a microscopic explanation of the specific binding of furanosides to proteins, which might be helpful in the potential design of novel inhibitors. We also provide a perspective on the choice of thermostats to properly sample the canonical distribution in simulations of this type of molecules.

Probing the Conformational Dynamics of Sheep Prion Dimers

Bilkiss B. Issack^{1,2,3}, *Mark Berjanskii*³, *David S. Wishart*^{1,4} and *Maria Stepanova*^{1,2}

¹National Institute for Nanotechnology NRC, Edmonton, Alberta

²Department of Electrical and Computer Engineering, University of Alberta

³Department of Computing Sciences, University of Alberta

⁴Department of Biological Sciences, University of Alberta

Prion diseases are fatal neurodegenerative disorders associated with a conformational change of prion proteins. The conversion of prion proteins from their normal cellular form (PrP^c) to the infectious scrapie state (PrP^{Sc}), in particular, is a key event according to the *protein-only* hypothesis. Subsequent aggregation and accumulation of amyloid through the central nervous system are responsible for cell death. It has been proposed that the conversion of PrP to PrP^{Sc} proceeds through the formation of a dimer but the infectious mechanism is still unknown to date. In order to obtain insight into the conversion of prion proteins, we investigate the conformational dynamics of sheep prion dimers through a recently developed approach [1,2]. Based on the theory of collective dynamics of proteins [1], the main appeal of the method lies in its potential to characterize long-living macromolecular conformations from relatively short molecular dynamics simulations. The approach has been successfully applied to investigate the structural domains and flexibility of prion proteins in their monomeric forms [2].

In this work, we have extended the applicability of the approach [2] to treat dimeric units and probe their collective dynamics. Molecular dynamics simulations on models of sheep prion dimer and monomer in explicit water under periodic boundary conditions at 300K were conducted with Gromacs 4.0.5. The monomer and dimer models were created from PDB entry 1UW3 before and after generation of the biological assembly with VMD program, respectively. In the chosen model of the prion dimer, the orientation of the helices is consistent with the structure of amyloids, in general, and prion fibril core, in particular, making it a reasonable precursor of prion oligomers and fibrils. Structural domains were identified by clustering essential coordinates generated by principal component analysis of the MD trajectories. The dependence of domain size on the dimensionality of the essential space that we have identified indicates that the sheep prion dimer is more rigid than the monomer. In addition, the structural domains show a clear separation in the correlated dynamics of helices H1 from that of region H2H3 of the dimer. The helix H1 is generally more flexible than the helices H2 and H3 in both the monomeric and dimeric forms of the sheep prion protein. Comparison of the main-chain flexibility profiles of the dimer and the monomer reveal a decreased flexibility of the H2H3 region upon dimerization, confirming that the dimerization may result in an increased conformational stability in comparison with monomeric prion proteins. Possible implications for the pathway to prion replication will also be discussed in the presentation.

The authors are grateful to Nikolay Blinov for his programming contributions to the domain clustering and flexibility analysis of monomers [2], and to the National Institute for Nanotechnology NRC and the Alberta Prion Research Institute for financial support.

1. M. Stepanova, *Phys. Rev. E* **76**, 051918 (2007).
2. N. Blinov, M. Berjanskii, D. S. Wishart and M. Stepanova, *Biochemistry* **48**, 1488 (2009).

Theoretical Study on the Geometric and Electronic Structures of M- BH₄ (M=Li and Na) clusters

*Yumie Kawasaki*¹, *Suehiro Iwata*³ and *Hidenori Matsuzawa*^{1,2}

¹Department of Life and Environmental Sciences, Chiba Institute of Technology, 2-17-1 Tsudanuma, Narashino, Chiba 275-0016, JAPAN

²Department of Chemistry, Center of Education, Chiba Institute of Technology, 2-1-1 Shibazono, Narashino, Chiba 275-0023, JAPAN

³Toyota Physical and Chemical Research Institute, Nagakute, Aichi 480-1192, JAPAN

Lithium boronhydride (LiBH₄) has been attracted attention as a fast lithium ion conductor of metal hydride system and a hydrogen storage material. There are few ab initio studies of the LiBH₄ clusters though many theoretical and experimental studies on the structural and electronic properties of the LiBH₄ crystal have been published. In this study, the geometric and electronic properties of the LiBH₄ and NaBH₄ clusters with the addition or detachment of an electron were examined. Calculation was performed using the 2nd-order Møller-Plesset perturbation (MP2) theory with the aug-cc-pVDZ basis set. The geometries of BH₄ (**1**), BH₄⁻ (**2**) and BH₄²⁻ (**3**) were examined. Next, the geometric and electronic structures of the M-BH₄ (**4**), [M-BH₄-M]⁺ (**5**), [BH₄-M- BH₄]⁻ (**6**) and [M-BH₄-M-BH₄] (**7**) (M=Li and Na) systems were investigated. Furthermore, each structure of the four model clusters, (**4**)- (**7**), was optimized after the addition or detachment of an electron. It is suggested that the BH₄ molecule (**1**) is composed of CH₂⁻ and H₂⁺. In the case of the electron detachment from the model clusters, an electron is removed from BH₄⁻. The B-H-B bridge as in a diborane is formed in (**7**) as shown in Fig.1 (a). On the other hand, after the addition of an electron, the small geometric change is found in the model clusters except (**5**). Figure 1 (b) shows the formation of the M-M bond after the electron addition to the model (**5**). The geometric and electronic changes in the model clusters are compared with those of the LiBH₄ and NaBH₄ crystals.

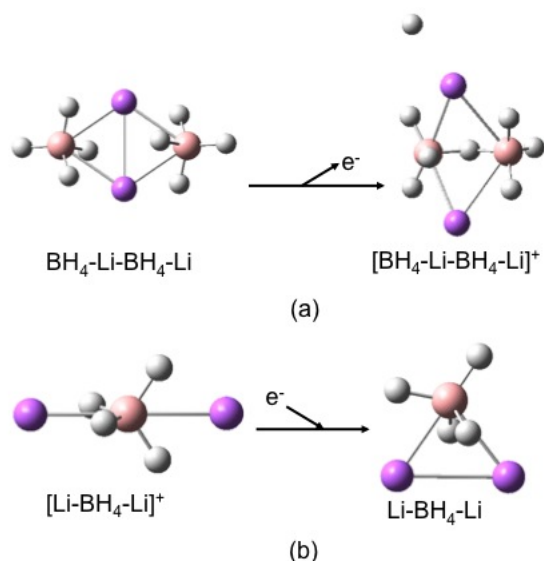


Fig. 1 Geometric changes with (a) the electron detachment from BH₄-Li-BH₄-Li (**7**) and (b) the electron addition to [Li-BH₄-Li]⁺ (**5**).

**Are There Any Magic Numbers for Water Nanodroplets, $(\text{H}_2\text{O})_n$, in the Range
 $36 \leq n \leq 50$**

Sergey Kazachenko and Ajit J. Thakkar

Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick,
Canada

Improved minima-hopping [1,2] followed by an evolutionary approach to optimization of hydrogen bond topologies [3] is used to locate putative global minima of TIP4P water clusters, $(\text{H}_2\text{O})_n$, for $36 \leq n \leq 50$. An analysis of the energies, hydrogen bond characteristics, and various other properties of the structures is presented. Clusters of 43, 46, and 48 water molecules appear to be significantly more stable than clusters of other similar sizes. The $(\text{H}_2\text{O})_{43}$ and $(\text{H}_2\text{O})_{48}$ clusters have a clathrate-like structure with a coiled water heptamer in a cage.

References

- [1] S. Kazachenko and A.J. Thakkar, AIP Conf. Proc. 1108 (2009) 90.
- [2] S. Kazachenko and A.J. Thakkar, Chem. Phys. Lett. 476 (2009) 120.
- [3] S. Kazachenko and A.J. Thakkar, Mol. Phys. 108 (2010) In press.

E-mail addresses: sergey.kazachenko@unb.ca, ajit@unb.ca

A36

Collocation Methods for the Boltzmann Equation; Hot Atom Relaxation and Ion Transport in Gases

Saheba Khurana, Bernie Shizgal and Mark Thachuk

Department of Chemistry, University of British Columbia, Vancouver, Canada

This is an approximate study conducted on an ensemble of tracer particles in an inert bath gas which is at equilibrium. In the ensemble, as a first approximation, the tracer and bath are treated as smooth hard spheres.

The ensemble in the system is described by the Boltzmann equation, and the inert bath gas is at equilibrium and is thus described by the Maxwellian distribution function. The right hand side (RHS) of the Boltzmann equation is the collision integral which is written in the form of the Wigner Wilkins kernel. The unknown distribution function, which we wish to obtain, is approximated by an expansion using cubic B-splines. These are splines constructed as polynomials of a given degree and smoothness, and are defined over a uniform grid over an interval of only four points.

The ensemble of tracer particles begins from a non-equilibrium, perturbed state, and the relaxation to equilibrium is observed. The approach to equilibrium conditions are observed at varying mass ratios and variations in temperature of tracer particles as well.

A37

Molecular Dynamics Simulation of the Transport Properties of the Rough Sphere Fluid

Olga Kravchenko and Mark Thachuk

Chemistry Department, University of British Columbia

We present a study of diffusion of a tracer particle in the rough sphere fluid that possess convertible energy of rotation. As the diameter of the tracer increases the theoretical description of the diffusion of the tracer changes from molecular (Enskog) to a hydrodynamic approach. For the latter case, the diffusion coefficient for a sphere depends on the fluid viscosity and the particular choice made for the boundary conditions at the surface of the sphere. It has been shown before that smooth hard sphere fluid adopts “slip” boundary conditions. The rough sphere fluid model allows for rotation of the individual particles and thus we can examine the effect of the rotational motion on the boundary conditions on surface of the tracer. We present a thorough calculation of the diffusion coefficient, as well as viscosity and thermal conductivity in the rough sphere fluid.

Application of the Constrained Variation DFT Method to Charge Transfer Excitations in Donor-Acceptor Complexes

Mykhaylo Krykunov and Tom Ziegler

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

We report in this work on an implementation of the constrained variation (CV) DFT method proposed in the paper by Ziegler et al. *J. Chem. Phys.* **130**, 154102 (2009) as an alternative to time dependent DFT (TDDFT) in studies of excited states. We have employed the Tamm-Dankoff (TD) approximation and included terms up to the 4th order in U . This level of approximation was previously termed CV(4)-DFT/TD. The second order of this theory in the TD approximation, i.e. CV(2)-DFT/TD, coincides with the regular TDDFT/TD.

We have calculated the one-electron excitation energies by this method and compared them to those calculated by TDDFT/TD, Δ DFT and Δ SCF-DFT. Comparison of the calculated results to the experimental charge-transfer excitations in various donor-acceptor complexes (where acceptor is a molecule of TCNE) shows that TDDFT/TD underestimates transition energies, while the CV(4)-DFT/TD overestimates them. The CV(4)-DFT/TD yields results that are very close to the Δ DFT scheme.

The Δ SCF-DFT method yields much better agreement with experiment. This emphasizes the importance of the relaxation of the Kohn-Sham (ground state) orbitals in the excited Slater determinants. However, for larger systems the role of the relaxation energy is smaller. Thus, the relaxation energy contribution decreases in the row of benzene, naphthalene and anthracene. We have also suggested in this work a method for the calculation of the relaxation energy within the CV(4)-DFT/TD framework.

Studies on Fluxionalism in Diborane and Related Species*Vibha Kumar*¹ and *P.P. Thankachan*²

¹Department of Chemistry, Indian Institute of Technology Roorkee(India), Vibha Kumar,
H.No.- 180/1, State Bank Colony Roorkee, Uttarakhand - 247667(India)

²Department of Chemistry, Indian Institute of Technology Roorkee(India), Department of
Chemistry, P.P. Thankachan Indian Institute of Technology Roorkee, Roorkee,
Uttarakhand - 247667(India)

Motivated by the reports on the transition state for the interchange of terminal and bridging hydrogens in AlBH_6 , we attempted to obtain the corresponding transition structure for B_2H_6 with three bridging hydrogens at various levels and using several basis sets. Since such a transition structure could not be characterized, we investigated the cases of ether-bound or amino-substituted diborane in which cases singly bridged transition structures were found. In the ionic species B_2H_5^+ and B_2H_6^+ tribridged transition structures were characterized. However in B_2H_6 , dissociation-recombination mechanism can at present be theoretically justified for proton scrambling.

A Molecular Superfluid: Non-Classical Rotations in Doped Para-Hydrogen Clusters

*Hui Li¹, Robert J. Le Roy¹, Pierre-Nicholas Roy¹, A. R. W. McKellar², Paul L. Raston³
and Wolfgang Jager³*

¹Department of Chemistry, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada

²Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

³Department of Chemistry, University of Alberta, Edmonton, Alberta N2L 3G1, Canada

When cooled to very low temperature, liquid helium exhibits the very peculiar property of flowing without friction or dissipation. This phenomenon, termed superfluidity, has been observed and well characterized in the bulk liquid phase. Until now, liquid ^4He and ^3He are the only substances that are known to exhibit superfluidity. Thus, there is considerable interest in finding superfluidity in other substances. Since para- H_2 molecules are spinless indistinguishable bosons, like ^4He atoms, they might also show superfluid behavior at low temperature. However, The triple point of hydrogen lies at 13.8 K, and its superfluid transition temperature has recently been estimated to lie below 2.0 K. Thus, the direct observation of superfluidity in a molecular system has still remained elusive.

Recent spectroscopic studies of molecules embedded in helium droplets suggest that a new route for investigating superfluidity of para- H_2 is to consider para- H_2 clusters doped with a single chromophore molecule (such as CO_2 , N_2O , or OCS). In order to confirm superfluid behaviour in molecular hydrogen, an experimental determination of the so-called superfluid response or non-classical rotational inertia is required. Here we report the first confirmation of molecular superfluidity in hydrogen clusters, based on the spectroscopic determination of the non-classical rotational inertia of para-hydrogen clusters doped with CO_2 or CO carbon dioxide. The main result of our study confirms earlier theoretical predictions that para- H_2 clusters could become superfluid, and lends further weight to experiments that have shown evidence of superfluidity of doped hydrogen clusters embedded in helium nanodroplets. Our results provide an understanding of the size dependence of the superfluid response of doped hydrogen clusters in terms of fractional filling of solvation rings and localization. The localization modulated superfluid response may be viewed as the nanoscale analogue of the insulating to superfluid transitions observed in cold gases, and further analysis may reveal a connection to the possible observation of “supersolidity” in helium.

Molecular Insights into the Formation Mechanisms of Gas Hydrate Crystals*Shuai Liang and Peter Kusalik*Department of Chemistry, University of Calgary, 2500 University Dr. NW, Calgary AB,
T2N 1N4

Molecular dynamics (MD) simulation has been proved to be a powerful tool in providing molecular details of solid/liquid interfaces and of crystal formation processes. We have employed a variety of MD methodologies to study the crystal growth of gas hydrate systems.

Our simulations have revealed that the CH₄ hydrates can be grown at very high rates (when compared to reported experimental values) if the necessary amounts of methane are provided to the growing interface. We have observed occasional formation of structure II crystal on existing structure I templates, facilitated by 5¹² 6³ cages. Various defects, including vacancies, water occupied cages, as well as doubly occupied cages, are identified in our simulations. The MD simulations also provide insights into the annealing mechanisms of CH₄ hydrates.

We have also performed crystal growth simulations of H₂S hydrates from both two-phase (hydrate crystal, H₂S aqueous solution) and three-phase (hydrate crystal, H₂S aqueous solution, and liquid H₂S) systems. The H₂S hydrates grown in these simulations exhibit comparatively low levels of defects. The structural transition involving 5¹² 6³ cages observed in CH₄ hydrates appears to occur with much lower frequencies in the growth of H₂S hydrates.

Theoretical Investigation of Sulfur-Assisted Oxidative Dehydrogenation of Alkane over Vanadia Catalyst

*John Lo*¹, *Tom Ziegler*² and *Peter Clark*^{1,2}

¹Alberta Sulphur Research Ltd., University Research Center, #6-3535 Research Road NW, Calgary, AB, T2L 2K8

²Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, AB, T2N 1N4

It has been observed previously that sulfur, as a milder oxidant than oxygen, facilitates the gas-phase oxidative dehydrogenation (ODH) of ethane, affording a higher product selectivity towards ethylene yet limiting the formation of CS₂ resulting from the over oxidation of ethane. Based on this observation, it is postulated that the addition of H₂S into the propane/O₂ mixture purged over strongly oxidizing vanadia catalysts would also lead to the production of propylene with high selectivity via the partial oxidation of H₂S that yields either S₂ or surface sulfide which triggers the ODH process. In this presentation, we will discuss from the theoretical viewpoint two possible reaction routes, namely gas-phase approach and surface approach, respectively, that describe the formation of propylene from propane. Comparison will be made between the results from the molecular simulations utilizing density functional theory and from the experimental work conducted in our group. Comments will also be drawn on the viability of the two proposed mechanisms pertaining to the sulfur-assisted ODH reaction of propane.

Theoretical Modeling of Solvation Structure and Gelation of an Oligomeric Electrolyte

Olga Lyubimova^{1,2}, *Xiangjun Liu*^{1,2}, *Sergey Gusarov*¹, *Alexander Kobryn*¹ and *Andriy Kovalenko*^{1,2}

¹National Institute for Nanotechnology, National Research Council of Canada, 11421 Saskatchewan Drive, Edmonton, Alberta, T6G2M9, Canada

²Department of Mechanical Engineering, University of Alberta, Edmonton, Alberta, T6G2G8, Canada

Based on the recent experimental results for sol/gel systems of poly(pyridinium-1,4-diyliminocarbonyl-1,4-phenylenemethylene chloride) (1Cl) [1,2], multiscale modeling of a number of the chemical and physical properties of 1Cl has been performed to study the solvation structure of the polyelectrolyte and the gelation process. It was shown [1,2], that the solubility and gelation ability of polyelectrolyte strongly depends on the counterion, type of solvent and salt addition. In this work we present the results of theoretical simulations for: (i) the solvation structure of 1Cl polyelectrolyte in aqueous solution; (ii) the counterion effect on the solvation structure of polyelectrolyte; and (iii) the effect of the polymer-solvent, solvent-solvent and polymer-polymer interactions. Structural parameters and charge distribution of the polymeric chains have been calculated at the quantum chemical level (PM6/COSMO). Within the frame of the 3D-RISM-KH integral equation theory of molecular liquids [3], the obtained data have been used for the subsequent calculations of the three-dimensional distribution functions of interaction sites of solvent molecules near the solute molecule of the polymer. The solvation structure of oligomeric electrolyte predicted by 3D-RISM-KH is in agreement with the results of molecular dynamics MD simulations we also carried out to study the polymer solvation structure as well as to characterize the gelation process. Using the modeling results obtained, we are developing a computationally amenable physical model capable of clarifying the cause of gelation and suitable for rational design of multifunctional gelators.

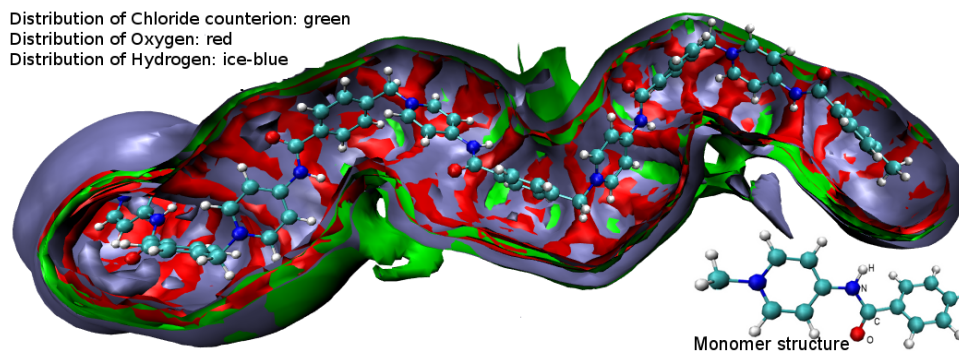


Figure 1. The probability density to find a specific solvent (water) site or counterion around the solute molecule of the polymer.

1. M. Yoshida, N. Koumura, Y. Misawa, N. Tamaoki, H. Matsumoto, H. Kawanami, S. Kazaoui, and N. Minami, *J. Am. Chem. Soc.* 2007, 129, 11039.
2. S. K. Kundu, M. Yoshida, and M. Shibayama, *J. Phys. Chem. B* 2010, 114, 1541.
3. A. Kovalenko in: *Molecular Theory of Solvation*, edited by F. Hirata, Kluwer, Dordrecht, 2003, 365 p., pp. 169-275.

Structure and Thermodynamics of Guanidinium-Water Clusters from First-Principles Molecular Dynamics Simulations

Chun C. Mak, Denise M. Koch and Gilles H. Peslherbe

Centre for Research in Molecular Modeling and Department of Chemistry and Biochemistry, Concordia University, 7141 Sherbrooke Street West, Montréal, Québec, Canada, H4B 1R6

Guanidinium salts are powerful protein denaturants widely used in experimental studies of protein stability and folding. The exact mechanism by which guanidinium cations denature proteins remains highly controversial, although there is consensus that the process involves complex intermolecular interactions between the macromolecule, guanidinium and water molecules. In this work, the solvation structure and thermodynamics of small to medium-sized guanidinium-water clusters are characterised to develop a clearer picture of the molecular interactions between guanidinium and water molecules. First-principles molecular dynamics simulations with umbrella sampling are used to compute the potential of mean force along the ion-to-water-cluster centre-of-mass distance coordinate, and the resulting probability distributions suggest that guanidinium resides primarily at the surface of small to medium-sized water clusters. The thermodynamic preference for the surface solvation state of small to medium-sized guanidinium-water clusters is a manifestation of the unusual hydrophobic nature of guanidinium and further lends credence to recent suggestions that guanidinium may bind to hydrophobic domains of biomolecules in aqueous solutions during the protein denaturation process.

Electron Solvation Dynamics in Photoexcited Iodide-Water Clusters*Chun C. Mak, Qadir K. Timerghazin and Gilles H. Peslherbe*

Centre for Research in Molecular Modeling and Department of Chemistry and Biochemistry, Concordia University, 7141 Sherbrooke Street West, Montréal, Québec, Canada, H4B 1R6

The photoexcitation of halides dissolved in polar solvents such as water results in the transfer of an electron from the anion to a diffuse, solvent-supported orbital. These halide charge-transfer-to-solvent excited states subsequently relax to produce solvated electrons, ubiquitous species that play important roles in numerous chemical and biochemical processes. Similar charge-transfer-to-solvent excited states also exist in iodide-water clusters of finite size, $\text{I}^-(\text{H}_2\text{O})_n$, which provide an interesting paradigm for the investigation of the roles played by the iodine atom and the solvent molecules in the electron solvation process. Recently, femtosecond photoelectron spectroscopy has been used to that effect, revealing complex excited-state dynamics that lead to stabilisation of the excess electron following photoexcitation of $\text{I}^-(\text{H}_2\text{O})_n$. It remains controversial whether the increase in the stability of the excess electron in excited $\text{I}^-(\text{H}_2\text{O})_n$ is the result of rearrangement of the water cluster moiety or iodine ejection from the cluster. In this contribution, *ab initio* molecular dynamics simulations and high-level quantum-chemical calculations are performed to unveil the complex rearrangement processes leading to the stabilisation of the excess electron in $\text{I}^-(\text{H}_2\text{O})_n$ and untangle the roles of the iodine and water molecules in $\text{I}^-(\text{H}_2\text{O})_n$ excited-state dynamics. Simulation results suggest that the gradual increase in the stability of the excess electron in photoexcited $\text{I}^-(\text{H}_2\text{O})_n$ is primarily due to the rearrangement of the water cluster moiety to bind the excited electron more tightly, although detachment of the iodine atom also affects the excited-electron distribution and is a crucial component of the process. Ultimately, these results will provide a clearer picture of electron solvation dynamics, both in gas-phase clusters and in bulk solutions.

Threshold Determination for Dissociation of $\text{H}_2(\mathbf{v},\mathbf{j}) + \text{H}_2(\mathbf{v}',\mathbf{j}')$

Margot Mandy

Program in Chemistry, University of Northern British Columbia, Prince George, British Columbia, CANADA V2N 4Z9

Rate coefficients are sensitive to the value of the threshold energy and to the values of the cross sections immediately above threshold. The energetic requirements of the process constrain the lower limit of the threshold, but dynamical effects can lead to an elevation of threshold energy above this.

State-specific dissociation rate coefficients are being calculated for $\text{H}_2(\mathbf{v},\mathbf{j}) + \text{H}_2(\mathbf{v}',\mathbf{j}')$ where $E(\mathbf{v},\mathbf{j})$ and $E(\mathbf{v}',\mathbf{j}')$ are less than 1 eV. The quasiclassical trajectory method was used on a chemically accurate potential for $\text{H}_2 + \text{H}_2(1)$. Examination of the potential indicates that the exchange channel is accessible at the dissociation limit. Earlier work (2) has shown the presence of an exchange channel at or below the dissociation limit allows randomization of total energy. Thus, no dynamic elevation of the threshold to dissociation is hypothesized and has been verified with restricted dimensionality calculations.

A preliminary full dimensional study using at least 80000 trajectories at each energy on a grid of 0.054 eV from the energetic threshold for dissociation to 5 eV above the threshold has shown that the cross sections near threshold are too small to be determined reliably at this batch size. Therefore it is necessary to model the excitation function near threshold in order to estimate the size of the cross section and the size of batch necessary to adequately determine them by a trajectory study. A number of approaches to determining the excitation function and the threshold are considered.

The resulting state-specific rate coefficients, γ , are parametrized (3) as a function of temperature over the range 1000 - 30000 K using: $\log_{10} \gamma(t) = a + bz + cz^2 - d(1/t - 1)$ where $t = T/4500$ K and $z = \log_{10} t$.

References

- (1) A. I. Boothroyd, P. G. Martin, W. J. Keogh, and M. J. Peterson, *J. Chem. Phys.* **116**, 666 (2002).
- (2) J. E. Dove, M. E. Mandy, N. Sathyamurthy, and T. Joseph, *Chem. Phys. Lett.* **127** (1987) 1.
- (3) M. E. Mandy, and P. G. Martin, *J. Chem. Phys.* **110** (1999) 7811.

Colchicine and Thiocolchicine Derivatives in Human Tubulin Isoforms: A Binding Free Energy Study

Jonathan Y. Mane and Jack Tuszynski

Department of Oncology, University of Alberta, Edmonton, Alberta, Canada T6G 1Z2

Many cellular activities are dependent on the dynamics of microtubule polymerization and depolymerization. Microtubules are polymers of α - and β -tubulin dimers. Small molecule ligands like paclitaxel, *Vinca* alkaloids, colchicine and podophyllotoxins are known to affect microtubule dynamics within the cell by binding to tubulin. These compounds bind to one of three distinct binding sites within β -tubulin, all of which have been identified crystallographically. Unfortunately, these molecules bind to tubulin indiscriminately, leading to the death of both cancerous and healthy cells. However, the existence and distribution of several β -tubulin isoforms in normal and cancerous cells provide a platform upon which to construct chemotherapeutic agents that can differentiate between cell types.

In this study, the focus is on the derivatives of colchicine and thiocolchicine. We performed binding free energy computations that aims at predicting differences between the binding energies of colchicine and thiocolchicine derivatives against several human β -tubulin isoforms. Binding free energies were evaluated using the method of linear interaction energy. The prediction of differences in binding provides us with invaluable information for subsequent design of better set of derivatives based on colchicine or thiocolchicine scaffold and/or analogues that can differentiate between cancer and non-cancer cells.

B1

DFT and Molecular Dynamics Investigations of Naphthalenediimide π - π Complexes as Building Blocks for Supramolecular Architecture

Jiri Mareda, Stefan Matile and Daniel Emery

Department of Organic Chemistry, University of Geneva, 30 quai Ernest Ansermet, 1211 Geneva 4, Switzerland

Supramolecular assemblies of *p*-oligopheny /naphthalenediimide (POP-NDI) and oligophenylethynyl/naphthalenediimide (OPE-NDI) diads are proposed to give access to the unique zipper architecture [1] with long lived photoinduced charge separation and an efficient photocurrent generation. In the present contribution we report quantum chemical investigations of substituted naphthalenediimides (NDI) and their π - π dimeric complexes as the essential building blocks for this architecture [2].

The capacity to form the π -stacks from the substituted NDI mono-mers is evaluated by the modeling of π - π dimer complexes. They are optimized with several DFT methods namely the Truhlar's M06-class functionals [3], which was reported to give good results for π - π interactions. Comparison of results obtained with several DFT and *ab initio* methods will be discussed. For the 2,6-dimethoxy-NDI, the computed properties of the dimeric complexes indicate particularly strong π - π interactions, which are reflected in the fairly strong binding interaction energy.

The QM results for NDI monomers and π - π complexes were also correlated with molecular dynamic simulations of the supramolecular zipper assemblies. MD simulations of topologically matching assemblies of OPE-NDI diads lead to ordered architectures, whereas topological mismatch in POP-NDI systems collapse and twist into more disordered, partially helical architectures.

[1] R. S. K. Kishore, O. Kel, N. Banerji, D. Emery, G. Bollot, J. Mareda, A. Gomez-Casado, P. Jonkheijm, J. Huskens, P. Maroni, M. Borkovec, E. Vau-they, N. Sakai, S. Matile, *J. Am. Chem. Soc.*, **2009**, *131*, 11106.

[2] N. Sakai, R. Bhosale, D. Emery, J. Mareda, S. Matile, *J. Am. Chem. Soc.* **2010**, *132*, 6923.

[3] Y. Zhao, D.G. Truhlar, *Acc. Chem. Res.* **2008**, *41*, 157.

B2

Calculation of Molecular Volumes Using Molecular Dynamics Simulations: Activation and Reaction Volumes

*Heather Martens*¹, *Nicholas Boon*¹, *Elna Deglinc*^{1,4}, *Essex Edwards*^{1,3}, *Paul Dance*¹ and
Noham Weinberg^{1,2}

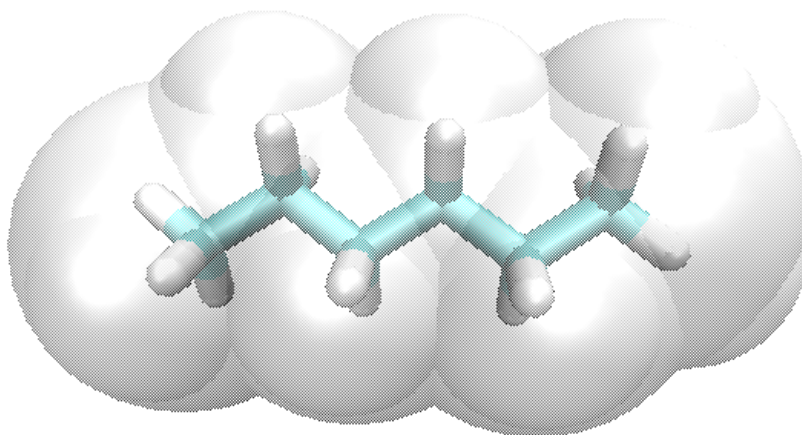
¹Department of Chemistry, University of the Fraser Valley, 33844 King Rd, Abbotsford,
BC Canada V2S 7M8

²Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, BC
Canada V5A 1S6

³Department of Computer Science, University of British Columbia, 2329 West Mall,
Vancouver, BC Canada V6T 1Z4

⁴Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton,
Ontario L8S4L8

Traditionally, the effects of pressure on reaction rates are expressed in terms of their pressure derivatives, known as activation volumes. According to transition state theory, activation volumes can be identified as the difference in volumes between the transition states (TS) and the reactants: $-RT(d \ln k/d P)_T = \Delta V_{TS} = V_{TS} - V_R$. Since reactant volumes V_R are readily available experimentally, the activation volumes ΔV_{TS} will provide a direct measure of the TS volumes V_{TS} . With a reliable computational method of relating the volumes for a molecular system to its geometrical parameters, the vast amount of experimental data on activation volumes in the literature could become an invaluable source for elucidating reaction mechanisms. We propose a method for the calculation of accurate activation volumes using molecular dynamics simulations of reaction systems in appropriate solvents.



B3

Theoretical Study on Aromatic Ring Formation Reaction of Metastable Diacetylene with 1,3-Butadiene in Titan's Atmosphere

Hidegori Matsuzawa^{1,2} and *Makoto Midorikawa*¹

¹Department of Life and Environmental Sciences, Chiba Institute of Technology, 2-17-1 Tsudanuma, Narashino, Chiba 275-0016, JAPAN

²Department of Chemistry, Center of Education, Chiba Institute of Technology, 2-1-1 Shibazono, Narashino, Chiba 275-0023, JAPAN

There is the thick atmospheric layer calling 'haze' in Titan, which is one of the satellites of the Saturn. It is well known that the diacetylene plays an important roll for the formation of the organic compounds in the haze. In 1998, Arrington et al. proposed the formation mechanism including five intermediates, of the benzene and phenylacetylene from metastable diacetylene and 1,3-butadiene in Titan's atmosphere, experimentally. In this mechanism, the triplet state for first four intermediates and the singlet state for the last intermediate are suggested. After the isomerization of the last intermediate, the benzene and phenylacetylene are formed from each isomer of the intermediate. In this study, the details of the ring formation mechanism from the metastable diacetylene with 1,3-butadiene were investigated theoretically, and the thermodynamics and the rate of reaction were examined. The stationary structures of the intermediates and the transition states were obtained by using the CIS method with aug-cc-pVDZ basis set. The reaction pathways were confirmed by the IRC calculation. Figure 1 shows the reaction pathway from the metastable diacetylene with 1,3-butadiene to benzene or phenylacetylene. It is found that the formation pathway of each benzene and phenylacetylene starts after the isomerization of **Int 3**. The triplet-singlet transition of **Int 5** occur and the newly intermediate, **Int 6**, are found, on both benzene (Bz) and phenylacetylene (Ph) formation pathways. The reaction enthalpies (ΔH) of Bz and Ph formations are -130.6 and -124.3 kcal mol⁻¹, respectively, under the Titan's condition. The rate-determining step is the reaction from **Int 5** to **Int 6**; the rate constant is 2.5×10^{-70} (Bz) and 1.5×10^{-101} (Ph) cm³ mol⁻¹ s⁻¹. Therefore, it is suggested that the benzene is predominantly produced rather than the phenylacetylene.

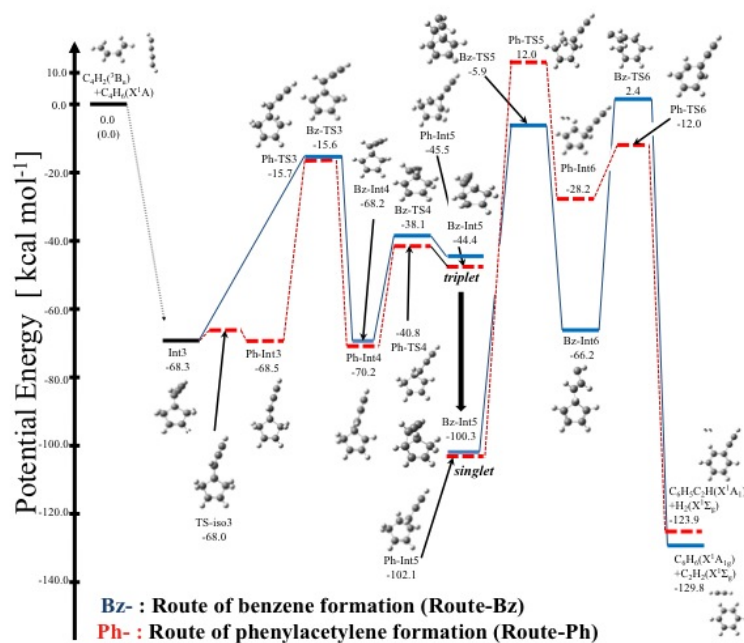


Figure 1 Potential energy diagram for $C_4H_2(^3B_1) + C_4H_6(X^1A)$ reaction. (Int3 \Rightarrow products).

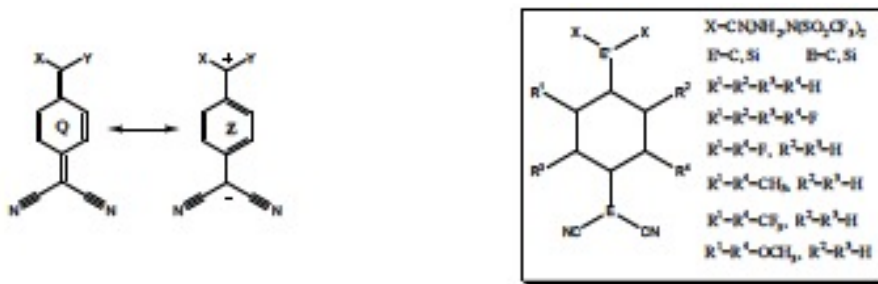
Assessing Quinoidal Structure in the Derivatives of Heavier Analogs of TCNQ

Robert Mawhinney

Department of Chemistry, Lakehead University, 905 Oliver Rd., Thunder Bay, ON

One of the most versatile molecules for the development of new molecular materials is 7,7,8,8-tetracyano-p-quinodimethane (TCNQ). One of its charge-transfer complexes (with tetrathiafulvalene) was the first true organic metal and several derivatives of TCNQ are considered precursors for second-order non-linear optics. These properties have been related to the relative proportions of quinoidal (Q) and zwitterionic (Z) contribution to the overall description of the molecule.

Recently, we began examining the feasibility of incorporating heavier atoms into the backbone of TCNQ and measuring the effects on the degree of quinoidal and zwitterionic character. In this poster, we will highlight our results from a Density Functional Theory study of a series of TCNQ derivatives containing a varying degree of silicon.



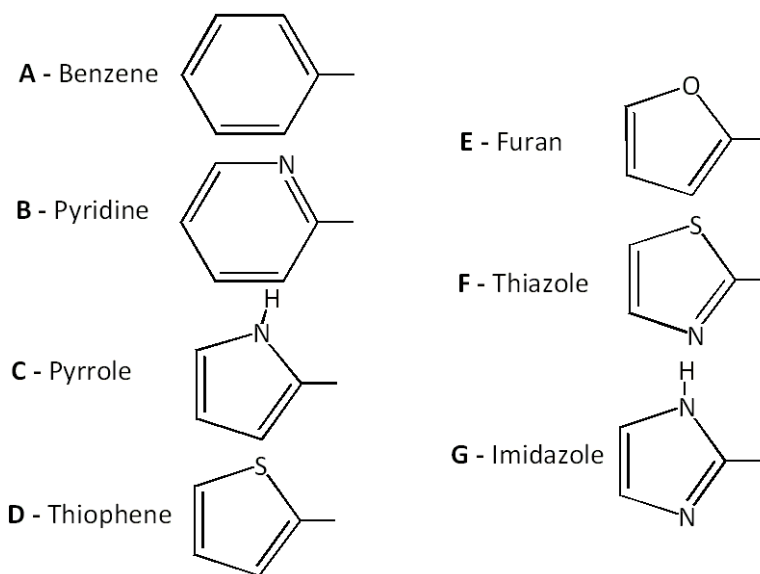
The relative proportions of quinoidal and zwitterionic contributions have been assessed using geometric factors, properties obtained from the Quantum Theory of Atoms in Molecules (QTAIM) and from weights provided by Natural Resonance Theory (NRT). The former two require the use of a reference system while the latter provides an absolute scale for assessing the other two approaches.

Rotational Barriers and Bond Controversy: A Computational Study of 28 Bisaromatic Systems

Robert Mawhinney and Rhiannon Kamstra

Department of Chemistry, Lakehead University, 905 Oliver Rd., Thunder Bay, ON

The torsional potential curves of bisaromatic species have been studied computationally in the past, particularly biphenyl. The Quantum Theory of Atoms In Molecules (QTAIM) uses the topology of the electron density to characterize bonding interactions.[1] QTAIM predicts bond paths between ortho hydrogen atoms in the planar biphenyl transition state.[2] The paths disappear as the equilibrium dihedral angle (≈ 40 deg.) is approached. The existence of these bond paths is controversial, as it contradicts the classical view that these interactions are repulsive and destabilizing.[3] To further characterize these types of bonding interactions, we examined the torsional potentials of 28 bisaromatic compounds containing 7 different subunits and performed a QTAIM analysis on each.



The potential energy curves can be grouped according to the number of distinct energy barriers and minima. Bond paths between ortho hydrogen atoms are found in planar biphenyl, 2,2'-bipyridine, phenyl-2-pyridine, phenyl-2-pyrrole, and phenyl-2-thiophene. All have type III potential curves, except bipyridine which has a type IV potential curve, and all are transition states on the surface. High ellipticity values suggest that these bond paths are unstable and on the verge of annihilation.

[1] Bader, RFW, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford (1990).

[2] Matta, CF; Hernandez-Trujillo, J; Tang, TH; Bader, RFW, *Chem. - Eur. J.* 9, 1940-1951 (2003).

[3] Poater, J; Sola, M; Bickelhaupt, FM, *Chem. - Eur. J.* 12, 2889-2895 (2006).

B6

Simple Models for Electron Correlation Energies in Atoms

Shane P. McCarthy and Ajit J. Thakkar

Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick E3B
5A3

Simple two- and three-parameter models that describe the variation of the electron correlation energy of atoms with atomic number are presented [1]. Despite their simplicity, these models have an accuracy comparable to the best available density functionals for the correlation energy [2].

References

- [1] S.P. McCarthy and A.J. Thakkar, Chem. Phys. Lett., in press (2010). Published online 2 June 2010. See <http://dx.doi.org/10.1016/j.cplett.2010.05.095>
- [2] A.J. Thakkar and S.P. McCarthy. J. Chem. Phys. 131 (2009) 134109.

Effect of Watson-Crick and Hoogsteen Base Pairing on the Conformational Flexibility of C8-Phenoxy-2'-deoxyguanosine Adducts

*Andrea L. Millen*¹, *Stacey D. Wetmore*¹ and *Richard A. Manderville*²

¹Department of Chemistry & Biochemistry, University of Lethbridge, 4401 University Drive
Lethbridge AB T1K 3M4

²Departments of Chemistry and Toxicology, University of Guelph, Guelph ON N1G 2W1

Aryl radicals can react with DNA to afford C8-aryl-2'-deoxyguanosine (dG) adducts. In nature, these bulky lesions can be generated due to the presence of carcinogenic arylhydrazines, polycyclic aromatic hydrocarbons, and phenolic toxins. Our research focuses on carbon-bonded C8-phenoxy adducts formed through both *ortho* and *para* bonding arrangements. The conformational flexibility of these adducts is likely related to their mutagenic potential, where other bulky adducts have been proven to exert their biological effects by inducing a *syn* orientation about the glycosidic bond in DNA helices. We have used computational chemistry to examine the conformational flexibility of the *ortho* and *para* C8-phenoxy dG adducts at the nucleoside and nucleotide levels. To ensure our methodology provides accurate results, we first benchmarked our nucleotide model by considering the relative stabilities of the *anti* and *syn* conformations of natural dG 5'-monophosphate. For the first time, we correctly predicted the conformational preference of this natural nucleotide by including implicit environmental effects and using a phosphate model that includes a sodium counterion. Using the same modeling approach, a slight preference for the *anti* orientation of both damaged bases was found. The small calculated energy differences between the *anti* and *syn* orientations imply that both conformations will be important in the DNA helix. Therefore, the Watson-Crick and Hoogsteen hydrogen-bond strengths of the damaged adducts paired with each of the natural bases were calculated to determine the influence of interstrand hydrogen bonding on the conformational preferences, as well as the likelihood of misincorporation opposite the lesions. Our calculations reveal that the Watson-Crick faces form the most stable base pairs, where cytosine is the preferred nucleobase for binding and therefore mispairing may not occur. However, the Hoogsteen face of the *para* phenoxy adduct was found to form stable complexes with multiple bases, which may explain the possible mutagenicity of this adduct. Further studies involving larger models of the damage incorporated in oligonucleotide strands are currently underway in our lab.

Hybrid Biosensors: Molecular Dynamics Simulations of DNA Hybridization

*Susanna Monti*¹, *Vincenzo Barone*², *Ivo Cacelli*³, *Alessandro Ferretti*¹ and *Giacomo Prampolini*²

¹Istituto per i Processi Chimico-Fisici (IPCF-CNR), via G. Moruzzi 1, I-56124 Pisa, Italy

²Scuola Normale Superiore, piazza dei Cavalieri 7, I-56126 Pisa, Italy

³Dipartimento di Chimica e Chimica Industriale - Universita' di Pisa, via Risorgimento 35, 56126 Pisa, Italy

Within the challenging and appealing field of the design and engineering of DNA sensors, a probe DNA molecule bound to a semiconducting surface can be exploited in recognition of a target DNA, as well as in identification of its damage and mutation.

One can therefore think of biochip devices based on the effects of possible hybridization between the single-strand DNA fragments, immobilized on the surface of an electrode through suitable functionalization procedures (probes), and the complementary oligonucleotide sequences present in solution (targets).

Understanding in detail the various steps of the hybridization mechanisms is extremely important when designing or improving DNA biosensors. To this aim classical molecular dynamics simulations and quantum mechanics calculations have been performed. Structure, dynamics and hybridization mechanism of DNA strands cross-linked to a functionalized silicon layer in solution have been investigated in detail. Molecular models, results of the simulations and comparison with experimental data (when available) are presented.

B9

Accurate and Reliable Calculation of Magnetic Interaction in Organic Diradicals

Susanna Monti¹, Vincenzo Barone², Ivo Cacelli³, Alessandro Ferretti¹ and Giacomo Prampolini²

¹Istituto per i Processi Chimico-Fisici (IPCF-CNR), via G. Moruzzi 1, I-56124 Pisa, Italy

²Scuola Normale Superiore, piazza dei Cavalieri 7, I-56126 Pisa, Italy

³Dipartimento di Chimica e Chimica Industriale - Universita' di Pisa, via Risorgimento 35, 56126 Pisa, Italy

Technological applications of magnetic materials in fast memories and electronic devices may benefit from the ability to rationalize and manipulate magnetic interactions in molecules and nanomaterials. From the theoretical point of view it is therefore important to be able to calculate spin-spin coupling terms through accurate and reliable methods at an acceptable computational cost.

In this perspective, in the framework of multireference configuration interaction, in the last few years we have been attempting to develop a computational strategy made by a balanced combination of molecular fragmentation, guided transformation of virtual orbitals and perturbation theory.

The application of the method to organic diradicals (nitroxides and nitronyl nitroxides) bridged by pi-system, such as polyene or aromatic fragments, give accurate and reliable values of the spin-spin coupling.

The details of the approach along with the results obtained will be reported.

Effects of Glycosylation on the Preferred Hydroxyproline Conformation

*Emmanuel B. Naziga*¹, *Stacey D. Wetmore*¹ and *Frank Schweizer*²

¹Department of Chemistry and Biochemistry, University of Lethbridge, 4401 University Drive, Lethbridge, AB, Canada, T1K 3M4

²Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2

Glycosylation is one of the post-translational modifications that can occur in proteins. In certain instances, this can cause backbone conformational changes as has been observed in experimental studies of glycosylated hydroxyproline. Specifically, although glycosylation of (2S,4R)-4-Hydroxyproline or Hyp has been shown to have no effect on the backbone conformation, glycosylation changes the trans/cis population and isomerization rate for the (2S,4S)-4-hydroxyproline (hyp) anomer. Structurally, Hyp prefers C^γ-exo puckering, while the dominant conformation of hyp is C^γ-endo puckering. These differences may result in different orientations of the sugar relative to the protein upon glycosylation. In this work, we perform molecular dynamics calculations in solution to study the conformations of novel $\alpha(\beta)$ -D-galactose O-linked Hyp and hyp derivatives. The overall goal is to rationalize experimentally observed conformational changes in these modified peptides.

Miller's Semi-Classical Transition State Theory: Implementation for Reactions of Polyatomics

T. L. Nguyen¹, J. F. Stanton² and J. R. Barker¹

¹Atmospheric, Oceanic, and Space Sciences, University of Michigan, Ann Arbor, MI 48109-2143, USA

²Department of Chemistry and Biochemistry, The University of Texas, Austin, TX 78712-0165, USA

In this work, we will describe a new algorithm for computing the cumulative reaction probability and/or partition function needed for the non-separable semi-classical transition state theory (SC-TST) described by W.L. Miller and coworkers [1,2]. The SC-TST automatically includes multi-dimensional tunneling and the effects of non-separable coupling among all degrees of freedom, including the reaction coordinate. The new algorithm is based on modifications of the three practical methods we described recently [3] for computing the sums and densities of fully coupled anharmonic vibrational states: exact-count, Monte-Carlo [4], and Wang-Landau [3,5,6] algorithms (the computer codes for state-counting can be downloaded freely from <http://aoss-research.engin.umich.edu/multiwell/>). The harmonic frequencies and matrix of anharmonicities required as input parameters for the calculations can be computed using standard quantum chemical software packages, such as Gaussian and CFOUR. The SC-TST method is practical for reaction systems containing dozens of atoms. Results obtained using the new algorithm will be presented and compared with other theoretical methods and with experimental data for reactions such as $\text{H}_2 + \text{OH}$, $\text{CO} + \text{OH}$, $\text{CH}_4 + \text{H}$, $\text{CH}_4 + \text{OH}$, and $\text{CH}_4 + \text{NH}_2$.

References:

- [1] W. H. Miller, R. Hernandez, N. C. Handy, D. Jayatilaka, and A. Willetts, *Chem. Phys. Lett.* 172 (1990) 62.
- [2] R. Hernandez and W. H. Miller, *Chem. Phys. Lett.* 214 (1993) 129.
- [3] T. L. Nguyen and J. R. Barker, *J. Phys. Chem. A* 114 (2010) 3718.
- [4] J. R. Barker, *J. Phys. Chem.* 91 (1987) 3849.
- [5] M. Basire, P. Parneix, and F. Calvo, *J. Chem. Phys.* 129 (2008) 081101.
- [6] F. Wang and D. P. Landau, *Phys. Rev. Lett.* 86 (2001) 2050.

**Chemical erosion of diamond thin-films by hyperthermal atomic oxygen:
Sometimes the assailant is the protector.**

*Jeffrey Paci*³, *Ze'ev Shpilman*¹, *Irina Gouzman*¹, *Eitan Grossman*¹, *L. Shen*², *Timothy Minton*², *George C. Schatz*⁴, *R. Akhvediani*⁵ and *Alon Hoffman*⁵

¹Space Environment Section, Soreq NRC, Yavne 81800, Israel

²Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT 59717, USA

³Department of Chemistry, University of Victoria, Victoria, British Columbia, V8W 3V6, Canada

⁴Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA

⁵Schulich Faculty of Chemistry, Technion, Haifa 32000, Israel

Diamond films can be created using a variety of chemical vapor deposition techniques. Because little is known about the durability of diamond in the space environment, we would like to have a better understanding of fundamental degradation processes of diamond in low-Earth orbit and in ground-based space environmental effects testing facilities, which is necessary for the future application of diamond-based devices in space technologies. Collisions between spacecraft and ambient atomic oxygen occur at hyperthermal energies because orbital velocities are so large (≈ 8 km/s). Therefore, studying the process in the laboratory is challenging. The development of accurate theoretical models is also demanding because large unit cells are required, and because the full elucidation of a collision process requires the development of a time-dependent picture of the events that take place. We explored this problem experimentally using a beam of hyperthermal atomic oxygen created using a laser detonation source. Extensive modeling of the collision events was also undertaken, using direct dynamics based on density functional theory and density functional-based tight-binding. Consistent with the atomic force microscope images of the exposed samples, the direct dynamics suggests that the (100) diamond surface can endure, while other surfaces chemically erode. The direct dynamics also suggests the mechanisms that could be responsible for the erosion processes, and the reason for the non-reactivity of the (100) surface.

B13

Simulating Strong-field Processes in Real Molecules

Serguei Patchkovskii and Michael Spannel

Steacie Institute for Molecular Sciences, NRC Canada, 100 Sussex Drive, Ottawa, Ontario,
K1A 0R6 Canada

We have recently proposed a new approach [1] for *ab initio* simulation of electron dynamics of molecules in atoms in molecules. The technique is based on a) use of non-antisymmetric “proxy” wavefunction and b) expansion in the mixed $N/(N-1)$ -electron basis of the neutral molecule and (possibly several) ion states. The effects of molecular potential on the continuum and correlations between the bound and continuum electrons are treated, permitting realistic simulations of electron dynamics in strong laser fields. We present some initial results obtained with the new technique, including angular-resolved ionization yields in strong fields and high-harmonic spectra of polyatomic molecules.

[1] M. Spanner and S. Patchkovskii, Phys. Rev. A 80, 083411 (2009)

B14

On the Structures of Asphaltene Molecules

Jeffery Perkins¹, Greg Dyck³, Essex Edwards^{1,4} and Noham Weinberg^{1,2}

¹Department of Chemistry, University of the Fraser Valley, 33844 King Rd, Abbotsford,
BC Canada V2S 7M8

²Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, B.C.
Canada. V5A 1S6

³School of Environment and Sustainability, Royal Roads University, 2005 Sooke Road,
Victoria, B.C., Canada V9B 5Y2

⁴Department of Computer Science, University of British Columbia, 2329 West Mall,
Vancouver, B.C. Canada V6T 1Z4

Asphaltenes are complicated hydrocarbon mixtures found in the heavy fraction of crude oils. While they are known to consist predominantly of various types of aromatic hydrocarbons, their exact molecular structures are unknown and have not been fully resolved. As a result, two competing and mutually exclusive models of asphaltene structures are being used. The opinions are split between the pericondensed model, according to which asphaltene molecules consist essentially of a single condensed polyaromatic system, and the archipelago model, which assumes that they contain multiple small-size aromatic units linked by hydrocarbon chains. In the present work we attempt to gain an additional insight into this issue by analyzing structural trends observed in sample sets of asphaltene molecules generated on a hexagonal grid by a random sequence of elementary steps of chain growth and crosslinking.

Stepwise Ordering of Water Molecules during Crystallization*Payman Pirzadeh, Eric Beaudoin and Peter Kusalik*Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary,
Alberta, Canada

A self-assembly process such as protein folding requires stepwise ordering of its components. It starts with a sampling of local environment to form short native bonds among amino acids and flows toward spatial communication of distant domains. Experimental measures show that probes sensitive to different ranges of order, i.e. secondary versus tertiary structure of a protein, will evolve in a certain order indicative of the presence of structural intermediate state(s). Furthermore, protein should surmount a free energy barrier between unfolded and folded state as a result of being an activated process. This picture has been summarized in a model known as the protein folding funnel. The latter model's interpretation is a non-trivial task due to the complexity of a protein molecule and its behavior. However, our molecular simulation studies show that simpler systems such as crystallizing water molecules could follow an analogous picture. Order parameters sensitive to various spatial ranges evolve in a certain pattern as a consequence of the presence of intermediate-range ordered water clusters (rings). As one approaches the ice-water interface, the population of certain sized rings and their positional correlation changes; for instance, the number of coupled five-seven member rings initially increases at the interface region and then vanishes in the solid phase while the number of coupled six-six member rings, which are the building blocks of ice, continually increases at the cost of other ring sizes. Furthermore, our analysis shows that there is a free energy barrier across the ice-water interface which water molecules will experience. Overall, we are able to show that formation of ice can also be seen to take place in stages where these stages correspond to specific levels of order as a folding funnel picture describes.

Investigation of Surface Effects in Chiral Adsorption using Parallel Tempering Monte Carlo Method

Tatiana Popa and Irina Paci

Department of Chemistry, University of Victoria, PO Box 3065, Victoria, BC, V8W 3V6

Chiral separation is a challenging task especially for pharmaceutical industries, where as products of synthetic chemistry, chiral drugs are manufactured and used as racemates. It is known that while one enantiomer have a therapeutic effect, the other one can be neutral or even toxic . A solid substrate may be used as a potential medium in promoting chiral resolution. The adsorption of a racemic mixture on a relative attractive surface leads in our case to formation of self assembled monolayers. A Parallel Tempering Monte Carlo algorithm with tempering over the temperature domains, done in canonical ensemble is used to examine the chiral adsorption of small (five atom) model molecules on a solid flat substrate. Our atomistic simulation show that surface geometry has an impact on adsorbed pattern and the formed clusters seem to commensurate with the underlying surface at low temperature. The encountered configurations consist of well segregated, enantioselected micellar structures. The quality of the resolution though depends highly on the complexity and the interplay of intermolecular interactions, and to a much lesser degree on the specifics of the surface potential.

Collective Dynamics in Prion Proteins: A Comparative Analysis of Disease-Prone and Disease-Resistant Species

Santo Poulose^{1,2}, *Mark Berjanskii*³, *David Wishart*³ and *Maria Stepanova*^{1,2}

¹National Institute for Nanotechnology, NRC, Canada.

²Department of Electrical and Computer Engineering, University of Alberta, Edmonton, Canada

³Department of Biological and Computing Sciences, University of Alberta, Edmonton, Canada

Understanding protein structural dynamics in connection with their functions is a highly challenging research topic of a great importance. The time scales of protein conformational transitions ($> \text{ms}$) by far exceeds the time scales ($\approx \text{ns}$) that can be studied using detailed all-atom molecular dynamics (MD) simulations with today's reasonable resources. Theoretically, an immediate solution to this problem is to use a coarse-grained approach that reduces the number of degrees of freedom to a few important ones, also known as the collective coordinates [1]. The collective conformational dynamics of proteins can provide key factors that govern protein functionality. These collective degrees of freedom represent dynamically correlated motion in proteins so that the protein may be divided into regions of relative rigidity and those of relative softness. A recent theoretical approach [2] provides essential methodology based on a generalized Langevin dynamics of the protein, for identifying these regions of dynamically correlated motion and to give a quantitative measure of relative flexibility of these regions. This formalism has recently been applied to the prion proteins (PrP). Prion proteins constitute the key element of the *protein only hypothesis* [4] that suggests a proteinacious infectious particle, the *prion*, as the infectious agent for Transmissible Spongiform encephalopathies (TSEs). The infectious form of the protein is a conformationally misfolded form of the normal prion protein suggesting a role of a conformational conversion in the pathogenesis. In the present study we perform a comparative analysis of the structural dynamics by analyzing the structural stability and back bone flexibility in prion proteins, as well as investigate the domains of correlated motion in PrPs of both disease-prone and disease-resistant species. We analyze the collective dynamics in prion proteins for elk, bovine, cat, hamster, and human, which develop prion diseases and also for turtle, frog and chicken, which do not develop prion diseases. We find that prions of most disease prone species, except for humans, exhibit a lower flexibility around the S2 - HB loop than those of prion disease resistant species. We also compare the numerical results with experimental NMR-derived flexibility profiles in prion proteins of these species, and find a reasonable, although not a complete, agreement. Based on the results obtained, we discuss the possible role of the flexibility of the S2-HB loop in the pathogenesis of prion disease.

The authors gratefully acknowledge Nikolay Blinov for his programming contributions to the code for the domain clustering and flexibility analysis [3] which has been used in this work, and the National Institute for Nanotechnology NRC and the Alberta Prion Research Institute for financial support.

[1] W. M. Brown, S. Martin, S. N. Pollock, E.A. Coutisias and J-P. Watson, *J. Chem. Phys.*, **129**,064118 (2008)

[2] M. Stepanova, *Phys. Rev. E.*, **76** , 051918 (2007).

[3] N. Bilnov, M. Berjanskii, D. S. Wishart and M. Stepanova, *Biochemistry*, **48** , 1488 (2009).

[4] A. Aguzzi and A. M. Calella, *Physiol. Rev.* **89** ,1105 (2002)

What is the General Base in the Mechanism of hUNG2 Action?

Jennifer L. Przybylski and Stacey D. Wetmore

Department of Chemistry & Biochemistry, University of Lethbridge, 4401 University Drive,
Lethbridge, Alberta T1K 3M4

One of the most common forms of damage to DNA is the deamination of cytosine to the RNA nucleobase, uracil. This lesion can lead to C:G to T:A transversions after two rounds of DNA replication. A majority of forms of life produce an enzyme, generally referred to as uracil-DNA glycosylase (UDG), which specifically removes uracil from DNA by cleaving the nucleobase-sugar (N-glycosidic) bond. There are at least three human proteins that fulfill UDG activity, where the most widely studied is hUNG2. While there exists a large amount of literature on the mechanism and kinetics of the hydrolysis reaction catalyzed by hUNG2 (and the *E. coli* homologue, eUDG), there is no conclusive evidence as to which residue acts as the general base to activate the nucleophilic water molecule. Although there is some experimental evidence that an active-site aspartate acts as a general base, a histidine residue exists in the active site that may also play an important role in water activation. This study uses an active-site model (> 600 QM atoms) to examine which of these two residues is more likely to activate the water and thereby catalyze this important DNA repair reaction. A two-layer ONIOM model (MPWB1K:PM3) is utilized to generate a three-dimensional reaction surface of the deglycosylation reaction in systems designed to allow transfer to a) the aspartate; or b) either the aspartate or the histidine. In addition, point mutations were carried out on both models and the effect of each mutation on the calculated barrier to hydrolysis is compared to experimental trends to aid in determining the model that best describes the experimental evidence.

NMR and Computational Studies Towards the Solution-State Conformation of Galactofuranosides

Mickey Richards and Todd Lowary

Department of Chemistry and Alberta Ingenuity Centre for Carbohydrate Science,
University of Alberta, Edmonton, AB T6G 2G2

Galactose can exist in two ring forms. The more common is the six-membered ring or pyranose, while the five-membered ring, or furanose, is less thermodynamically stable. In mammals, galactose is only found in the pyranose form, while it is commonly found in both forms in many pathogenic organisms, including *Aspergillus fumigatus*, *Klebsiella pneumoniae*, and *Mycobacterium tuberculosis*. Additionally, in many of these organisms, galactofuranose (Galf) is essential for viability.

We propose a detailed understanding of conformational properties of Galf-containing polysaccharides is critical for exploiting them as therapeutic targets. The furanose ring is much more flexible than the pyranose ring, and conformational models of the former are not well refined. We will present work towards an improved solution-state model of Galf, using a combination of NMR experiments, DFT calculations, and molecular dynamics (MD) simulations. Specifically, newly derived Karplus-like relationships for proton-proton and proton-carbon three-bond coupling constants will be shown. These new equations have been used, in combination with the experimental three-bond couplings, to determine the conformation of both methyl alpha- and beta-D-Galf in solution. The DFT calculations and the experimental NMR data together are necessary to parameterize Galf for use in MD simulations with AMBER/GLYCAM06. Initial results from MD simulations will be presented.

Effective Fragment Potential (QM/EFP) Study of C-H Bond Activation of Methane by $[\text{PtCl}_4]^{2-}$ Complex in Aqueous Solution

William Rocha and Júlio Da Silva

Departamento de Química, ICEX, Universidade Federal de Minas Gerais, 31270-901, Belo Horizonte, Minas Gerais, Brazil.

Alkanes are the major constituents of natural gas and petroleum. However, efficient, selective, and direct functionalization of hydrocarbons under mild conditions remains a difficult challenge to chemists even today [1]. A large number of organometallic complexes are now known to be capable of reacting with alkanes, activating (breaking) the C-H bond [2]. One of the first homogeneous catalysts for C-H activation was discovered by Shilov et al in 1969 when they found that the $[\text{PtCl}_4]^{2-}$ complex could catalyze H-D exchange of alkanes in acidic aqueous solution [3]. So, motivated by the particularities existing in the processes of C-H bond activation of alkanes, we investigated the main mechanistic aspects of the Shilov reaction involving methane activation by $[\text{PtCl}_4]^{2-}$ complex in aqueous solution, using the hybrid quantum mechanics/effective fragment potential (QM/EFP) approach [4]. We will show and discuss the main results related to structural characteristics, energetic proprieties, reaction mechanism and charge distribution calculated along the reaction coordinate using the QM/EFP approach. We will also discuss about our strategy used to build the initial EFP water cluster, based on an initial Classical Monte Carlo Simulation followed by analysis of the center-of-mass radial pair distribution function.

[1] Labinger, J. A.; Bercaw, J. E.; *Nature*, 2002, 417, 507.

[2] See, for example, Shilov, A. E.; Shul'pin, G. B.; *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*, 2000. Kluwer Academic, Dordrecht.

[3] Gol'dshleger, N. F.; Tyabin, M. B.; Shilov, A. E.; Shteinman, A. A.; *Khim, Zh. F.*; *Engl. Transl.*, 1969, 43, 1222.

[4] Adamovic, I.; Freitag, M. A.; Gordon, M. S.; *J. Chem. Phys.*, 2003, 118, 6725.

DFT Interband Optical Properties of Metal-Polymer (Ag/PVDF) Nanocomposites: Size, Shape, % Volume and Anisotropy Effects

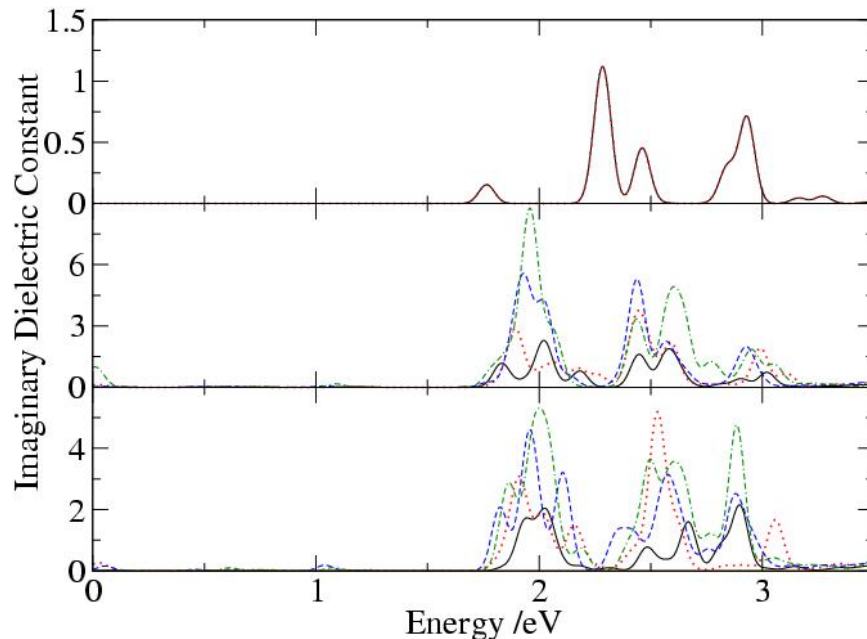
Christopher Rowan and Irina Paci

Department of Chemistry, University of Victoria, P.O. Box 3065, Victoria, BC, V8W 3V6

Metal-polymer nanocomposite materials have tunable optical responses depending on metal inclusion size and shape with low volume percent in a host polymer matrix. The effect of these factors, as well as the anisotropic response from a polarized incident electric field over the optical energy range has been studied with a model system of PolyVinylidene Fluoride (PVDF) with up to 1250 atoms, and Ag clusters ranging from 12-32 atoms: as low as 1.6 %vol Ag. The imaginary part of the dielectric constant was calculated from dipolar interband transitions within DFT, after packing the structures under PBC to approximate densities with MD. The frequency dependent real part of the dielectric constant, complex refractive index, absorption coefficient, conductivity and reflectance were then determined. A variety of inclusions were examined, including: energy minimized amorphous 12 and 13 atom clusters; crystalline 13 atom cuboctahedron and expansions thereof with 2, 4 and 6 atoms to form clusters of 15, 17 and 19 atoms; a variety of rods made of stacked (100) or (111) sheets; and a larger sphere of 28 atoms.

Calculations show that PVDF with no inclusion is an insulator with a band gap of approximately 6eV. The effect of the inclusion introduces electronic energy levels most notably in the range of 0.5 - 3.5 eV. Increased volume fractions of Ag generally increased the magnitude of the imaginary part of the dielectric constant, and the peak positions were dependent on the inclusion size and shape. As structures deviated from spherical, anisotropic effects were observed.

As an example, the figure below shows the directional optical properties and % volume effects from a 13 atom Ag cuboctahedron in PVDF. Bottom and middle subplots: polarization along principal (z-) and minor (x-) axes, respectively. Upper subplot: directional response of Ag13 cluster in vacuum. Increasing % volume (or polarization direction for Ag13 in vacuum): solid black line–1.7 (z); dotted red line–2.9 (x); dashed blue line–4.0; dot-dashed green line–5.1; solid yellow line–0.



The Topology of the Ice-Water Interface from Molecular Simulations

Dmitri Rozmanov and Peter Kusalik

Department of Chemistry, University of Calgary, Alberta, Canada

The dynamics, energetics, and structure of interfaces are key to understanding heterogeneous processes as well as processes of self-organizations and disordering of matter. Specifically, the ice-water interface is very interesting because of the great importance of water, and because it can be seen as a component of the quasi-liquid-layer of ice-air interfaces, which has great atmospheric relevance.

In this work the topology of the (0001) Ih ice-water interface was obtained and visualized from the results of classical molecular dynamics simulations. The interface surface was defined and obtained as an isosurface of a spacial continuous profile function derived from discrete molecular dynamics trajectories. The interface was studied at the melting temperature (T_m) and also at the temperature of maximum growth rate ($T_m - 10$ K). The TIP4P-2005 effective potential model was used to represent water.

The interface surfaces obtained using different properties of the system, energy, mobility, and structural order, were examined. The differences in topologies obtained from different measures and topological features are analyzed and discussed. Possible applications of topological information are also proposed.

Computational Modeling of DNA-Protein Noncovalent Interactions Found in DNA Repair Enzymes

Lesley Rutledge and Stacey Wetmore

Department of Chemistry and Biochemistry, University of Lethbridge, 4401 University Drive, Lethbridge, AB, T1K 3M4

The interactions between DNA and proteins are vital for a variety of fundamental biological processes. For example, repair of DNA damage relies on interactions between DNA and protein components to selectively identify and remove only damaged nucleobases. Of particular interest are the interactions between DNA and proteins that govern the enzymatic repair of a common type of DNA damage, DNA alkylation, which leads to cationic nucleobases. Crystal structures of enzymes that facilitate this repair (the DNA glycosylases) indicate that alkylated nucleobases may be held in the active site through contacts with aromatic amino acid residues. However, very little is known about the role of these aromatic amino acids or their involvement in the mechanism for this repair pathway.

The interactions used by the DNA glycosylases to recognize alkylated DNA bases have been proposed to be weak noncovalent π - π stacking and T-shaped interactions. However, stacking and T-shaped interactions between the π -systems of DNA and protein fragments are not well characterized in the literature. Therefore, the present work uses *ab initio* calculations to study these interactions between natural DNA and RNA nucleobases or damaged cationic nucleobases and the four aromatic amino acids. Our calculations reveal the magnitude of these interactions, as well as the attractive nature of the bonding present between these important biological building blocks. Our benchmark data set has been used to identify additional computationally-efficient (density functional theory) methods that are capable of describing stacking and T-shaped interactions, which can be used in large-scale (ONIOM(QM:MM)) modeling of the mechanism-of-action of these unique DNA repair enzymes.

A Theoretical Study of Magnetic Coupling in Electrides*Ilya G. Ryabinkin and Viktor N. Staroverov*Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7,
Canada

Electrides are stoichiometric solids in which near-free electrons occupy lattice cavities and interact through the connecting channels. These materials have interesting magnetic properties that are strongly influenced by the geometry of the cavity-channel network. The simplest model of an electride is a “dogbone”-shaped box: a pair of electrons each of which is confined in a spherical cavity and interacts with the other electron through a cylindrical channel. We developed a general method for solving the Schrödinger equation for such model systems and used it to rationalize the observed dependence of the Heisenberg exchange coupling constant J on the length and diameter of the cavity channel. We also discuss simple functional relations between J and the geometrical parameters of the channel which make it possible to predict the coupling strength without full-scale calculations.

Nonadiabatic Dynamics and Excited State Population Revivals in DABCO*Michael Schuurman, Andrey Boguslavskiy and Albert Stolow*Steacie Institute for Molecular Sciences, National Research Council, 100 Sussex Dr.,
Ottawa, CANADA, K1A0R6

Employing standard approaches for characterizing the branching space of a conical intersection, it is possible to predict which molecular motions most efficiently facilitate non-adiabatic transitions. An even more complete description of the intersection topography is achieved via the construction of model vibronic potentials using ab initio electronic structure methods. These vibronic Hamiltonians may be subsequently used to simulate absorption or photoelectron spectra involving coupled electronic states, or similarly, time-dependent wavepacket behaviour. These techniques are employed in the analysis of recently measured time-resolved photoelectron spectra for 1,4-diazabicyclo[2.2.2]octane (DABCO). Following the initial excitation of the singlet S2 state and subsequent decay to the S1 state, this molecule appears to display a revival in excited state population. A Fourier analysis of the time-resolved spectra is performed to reveal the characteristic revival frequencies. An analysis of the low-energy seams of conical intersection between these states identifies the relevant coupling modes and assigns the time scales of revival to beat frequencies that correspond to the splitting of near e' symmetry vibrational modes in the Jahn-Teller distorted S2 state. The size of this system, and the correspondingly large number of internal degrees of freedom, make for a novel result in which intramolecular vibrational redistribution (IVR) processes are slowed by the reduced coupling between vibrational modes engendered by the high-symmetry of this rigid-cage molecular species.

TDDFT Gradients- Excited State Geometry Optimizations with ADF*Michael Seth and Tom Ziegler*Department of Chemistry, University of Calgary, 2500 University Dr NW, Calgary, AB
T2N 1N4

We have implemented a form of the TDDFT gradients methodology proposed by Van Caille and Amos (1-2) and Furche and Ahlrichs (3) into the Amsterdam Density Functional (ADF) program. The implementation allows geometry optimizations of excited states to be performed with a range of functionals (GGA and hybrid) and with several forms of TDDFT (closed shell, open shell, spin-flip). Some details of the implementation are presented along with a few illustrative applications. The applications focus areas where the more novel spin-flip excitations are particularly useful.

- (1) C. Van Caille and R.D. Amos Chem. Phys. Lett. 308, 249-255 (1999)
- (2) C. Van Caille and R.D. Amos Chem. Phys. Lett. 317, 159-164 (2000)
- (3) F. Furche and R. Ahlrichs J. Chem. Phys 117, 7433-7447 (2002)

Computational studies of NO diffusion in hemoglobin: Relevance in vasodilation

Mariya Shadrina, Denise Koch, Ann English and Gilles Peslherbe

Centre for Research and Molecular Modeling and Department of Chemistry and Biochemistry, Concordia University, Montréal, QC

Hemoglobin (Hb) is the most abundant component of red blood cells (RBCs). This protein transports Fe(II) heme-bound oxygen (O_2) from the lungs to the tissues, and the cooperative binding of O_2 is accompanied by a transition from a low-affinity, unligated T-state to a high-affinity, ligated R-state of the protein. Regulation of blood flow in the microcirculation is controlled by physiological oxygen (O_2) gradients in the vessels, which undergo vasodilation and vasoconstriction [1]. Endothelium-derived NO is a principal activator of vasodilation and binds to the unligated Fe(II) heme of Hb. On aeration, Hb changes conformation from the T- to R-state and some of the Fe(II)-bound NO undergoes transfer to Cys β 93, forming S-nitrosohemoglobin (SNO-Hb), which is proposed to be vasoactive [2]. The reported crystal structure of SNO-Hb [3] suggests that S-nitrosation occurs exclusively on the surface Cys β 93 residues, but the mechanism of NO transfer from the heme to the thiols is unknown. The intramolecular diffusion of NO molecules from the heme to Cys β 93 was investigated by molecular dynamics simulations. Diffusion pathways in both the α - and β -subunits were examined in detail for the different conformational states of the Hb tetramer. The tunnels within the protein were found to be independent of the heme-ligation state but not the exits or the escape times of the NO molecules. The largest difference observed was for the β -subunits in the T- and R-state Hb. NO quickly escaped from the β -subunit to the central cavity between the subunits in T-state Hb whereas NO remained within the β -subunit in R-state Hb. Importantly, no direct pathway for NO transfer between the heme and Cys β 93 was found in any of the Hb states examined. The relevance of intramolecular NO diffusion in Hb to its role in vasodilation are discussed in light of the computational results.

1. T. J. McMahon et al., *Nature Medicine*, 2002, 8, 711-717.
2. J. Laterreur, A. M. English, *Journal of Inorganic Biochemistry*, 2007, 101, 1827-1835.
3. N. L. Chan, P. H. Rogers, A. Arnone, *Biochemistry*, 1998, 37, 16459-16464.

Stability of Hydrocarbons of the Polyhedrane and Para-Cyclophane Families: Matching Exchange and Correlation Density Functionals

Grigory A. Shamov^{1,2}, *Peter H. M. Budzelaar*¹ and *Georg Schreckenbach*¹

¹Department of Chemistry. University of Manitoba, Winnipeg MB Canada R3T 2N2

²Dutch Polymer Institute (DPI), P.O. box 513, 5600 MB Eindhoven, The Netherlands

The stabilities of polyhedral hydrocarbons, such as dodecahedrane $C_{20}H_{20}$ and its C_nH_n ($n=12,16,24$) analogs were studied computationally, by comparison with the corresponding isomeric hydrocarbons. In addition, a comparison was made of isomeric, well-studied hydrocarbons of similar size, specifically the set of C_nH_n cyclophanes ($n=16,20,24$) and a cyclophane-like $C_{12}H_{12}$. Results obtained by a variety of Density Functionals were tested against the SOS-MP2 method.

We show that, for the set of polyhedranes, the DFT results vary widely with the choice of the density functional. In particular, large discrepancies with SOS-MP2 were found for the functionals that are based on the B88 and B86 exchange and the LYP correlation parts. The problem is not related to the presence of the smaller carbocycles in the $C_{12}H_{12}$ and $C_{16}H_{16}$ polyhedranes. We demonstrate that these errors stem from the B88 (and certain other, like B86, G96) exchange, and are not compensated by Colle-Salvetti-based GGA correlation functionals such as LYP, OP, and TCA. However, they can be overcome by the PBE correlation functional based on the PW92 uniform electron gas (UEG) parametrization. Long-range hybrids LC-BOP, LC-BLYP perform much better than the parent GGAs.

The set of cyclophanes show a completely different performance as compared to the polyhedranes. There, the LC-type functionals do not give any improvement, but DFT-D corrected BLYP-D performs very well. We conclude that, while for polyhedranes delocalization errors from exchange dominate, for cyclophanes the correlation/overlap-dispersion interactions are important. The OPTX exchange functional shows significantly lower errors compared to B88 and G96; its combinations like OLYP and especially KT3 perform well for the both test sets.

This work was supported by and is part of the Research Programme of the Dutch Polymer Institute (DPI), Eindhoven, The Netherlands, project #641.

Hydroboration of Cyclopropane: Ab Initio and DFT Calculations

Satya Prakash Singh and P.P. Thankachan

Department of chemistry, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand-247667 (India)

The hydroboration of cyclopropane was experimentally studied by W.A.G. Graham and F.G.A. Stone and Bruce Rickborn and Stanley E. Wood. The reaction has not so far been investigated theoretically. We have investigated the reaction at RHF, MP2 and DFT levels and characterized the transition structures at each level using 6-31G(d,p), D95V(d,p) and cc-pVDZ basis sets. The barriers obtained by MP2 and DFT/B3LYP calculations are all less than 12 kcal/mol while that at RHF level are much higher. Structural parameters for the transition structure is reported.

Email: satya0983prakash@rediffmail.com

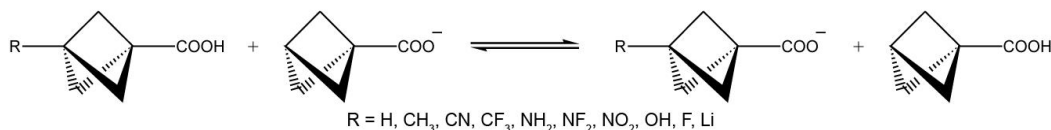
The Inductive Effect: A Quantum Theory of Atoms in Molecules Perspective

Ashlyn Smith and Robert Mawhinney

Department of Chemistry, Lakehead University, 905 Oliver Rd., Thunder Bay, ON

Many phenomena in chemistry are explained using substituent effects. Despite their widespread use, the foundations remain empirical in nature. Attempts have been made to recreate experimental relationships, but development of a purely quantum basis for substituent effects has been decidedly unsatisfactory. We have focused on the inductive effect (the transmission of charge through bonds [1]) in derivatives of bicyclo[1.1.1]pentanoic acid to develop a method for the prediction of the effect in any system. This model has been chosen due to the impossibility for conjugation, the elimination of any steric effects, and the rigidity of the carbon backbone.

The Quantum Theory of Atoms in Molecules (QTAIM) [2] has been used as the main tool in this investigation. QTAIM analyzes the topology of the electron density in a molecule, and is therefore perfectly suited to the study of the inductive effect. Several molecular properties have been correlated to the energies for the isodesmic reaction shown below, which is a measure of the inductive effect. As expected, the energy of the acidic hydrogen correlates very well to the reaction energy ($r^2 = 0.993$). Some properties associated with the carbonyl oxygen of the acidic species are also very good: the intraatomic dipole moment contribution ($r^2 = 0.991$) and the average number of electrons localized on the atom ($r^2 = 0.990$).



[1] Muller, P. *Pure and Applied Chemistry* 66 (1994) 1077.

[2] RFW Bader, *Atoms in Molecules: A Quantum Theory*. Oxford University Press, Oxford, 1990.

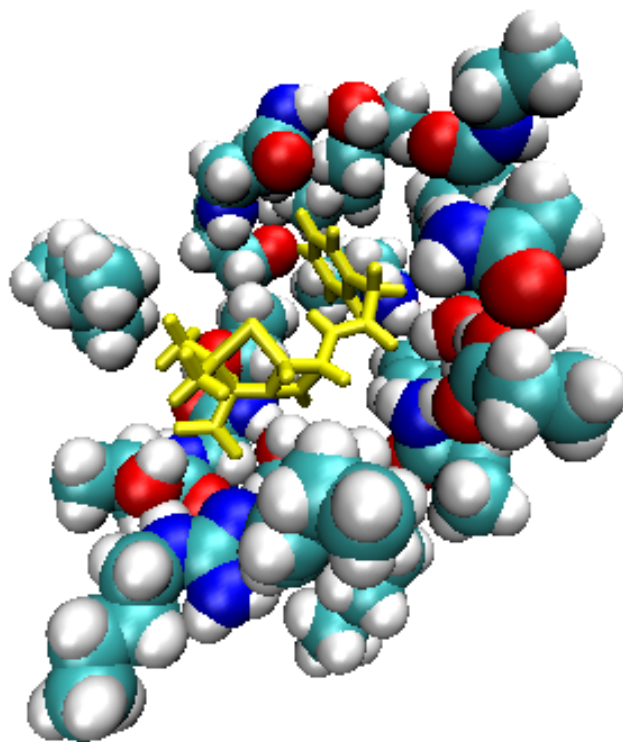
Binding of Penicillin-type Antibiotics to the Active Sites of Penicillin-binding Proteins: A Comparative Computational Study

Jacob Spooner¹, Saul Wolfe² and Noham Weinberg^{1,2}

¹Department of Chemistry, University of the Fraser Valley, 33844 King Rd, Abbotsford, BC Canada V2S 7M8

²Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, B.C. Canada. V5A 1S6

Penicillin antibiotics achieve their antibacterial effect by inhibitive binding to a family of enzymes located in the bacterial cell membrane. Better understanding of the molecular mechanism of such binding is crucial to our ability to design new drugs. We report here the preliminary results of our quantum mechanical and molecular dynamics studies of the interaction between a series of antibiotics from the penicillin family with the active sites of the two penicillin-binding proteins, DD-Carboxypeptidase-Transpeptidase of *Streptomyces* (R61) and Penicillin Binding Protein 2a from Methicillin-Resistant *Staphylococcus aureus* (PBP2a).



An Analytical Time-Correlation Function Treatment for Vibronic Transitions*Jason Stuber and Marcel Nooijen*

Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada

A time-correlation function (TCF) treatment of vibronic transitions between adiabatically parametrized potential energy surfaces is presented. By using a coherent state representation, under the assumption of Duschinsky rotated harmonic potential energy surfaces, one can obtain an analytical expression for the TCF. This expression is formally exact, requiring no mode or excitation truncation, and can be evaluated in $O(N^3)$ time for an N -mode vibrational surface. The desired spectral profile can then be obtained in practice through a discrete Fourier transformation after a one-dimensional time-sampling of the TCF. This procedure circumvents the historical bottleneck which has hindered the investigation of larger molecular systems, namely the evaluation and storage of vibrational overlap integrals. For illustration purposes this prescription is specialized to Franck-Condon (FC) transition processes.

The general approach detailed within is sufficiently flexible to be utilized within other vibronic transition processes, such as in circular dichroism (CD) and resonance Raman, and can be extended to also include anharmonic corrections.

Direct Approach to Gravitation and Electrostatics*Dage Sundholm and Sergio A. Losilla*

Department of Chemistry, P.O. Box 55, FIN-00014 University of Helsinki, Finland

The Direct Approach to Gravitation and Electrostatics (DAGE) algorithm is an accurate, efficient, and flexible method for calculating electrostatic potentials. We show here how the algorithm can be extended to consider systems with many different kinds of periodicities, such as crystal lattices, surfaces, or wires. The accuracy and performance are the same for periodic and aperiodic systems. The electrostatic potential for semi-periodic systems, such as defects in crystal lattices can be obtained by combining periodic and aperiodic calculations. The method has been applied to an ionic model system mimicking NaCl and to a corresponding covalent model system. We have also developed a computational scheme for performing accurate numerical calculations of electrostatic potentials using molecular charge densities. The molecular domain is divided into spherical atomic regions and the complementary density. The electrostatic potentials of the atomic domains are obtained by one-dimensional (1D) numerical integration. The electrostatic potential originating from the difference between the total molecular electron density and the sum of the charge densities of the spherical atomic regions is obtained by three-dimensional (3D) numerical integration of the Coulomb expression using the DAGE method. The applicability of the method is demonstrated by calculating the electrostatic potential for a water droplet with high accuracy.

Conformational Analysis of Arabinofuranosides

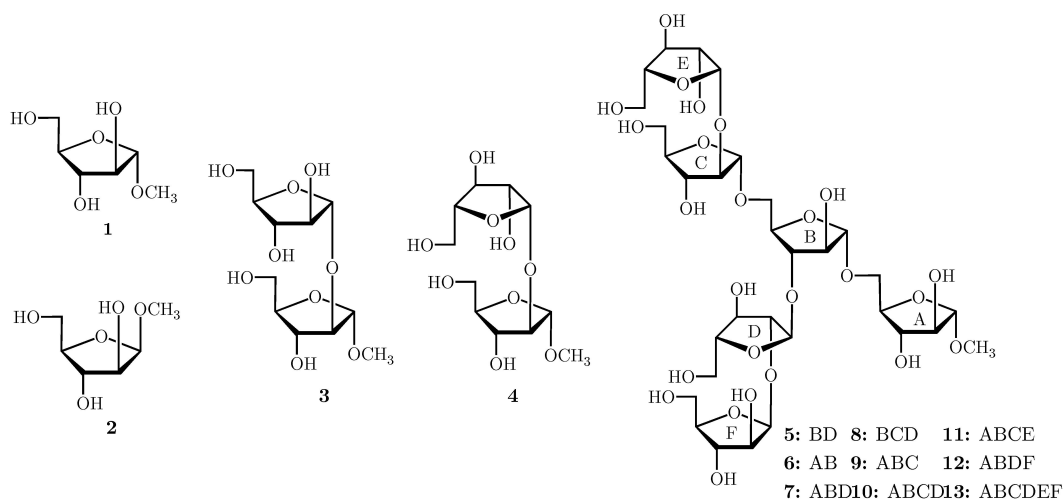
*Hashem Taha*¹, *Pierre-Nicholas Roy*² and *Todd Lowary*¹

¹University of Alberta, Edmonton, Alberta, T6G 2G2, Canada

²University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada

Furanosides are important constituents of a number of glycoconjugates from many microorganisms. In particular, arabino- and galactofuranosides make up a major component of the complex cell wall structure of *Mycobacterium tuberculosis*, the organism responsible for tuberculosis. The highly flexible nature of these furanosyl moieties is believed to contribute significantly to their role in biological processes. Therefore, an understanding of their conformational preferences is an important area of research.

The conformational determination of these ring systems is difficult due to their great flexibility, as they can adopt various envelope and twist conformations separated by low energy barriers. An important tool in the assessment of the solution conformations of these furanose ring systems has been a computer program named PSEUROT.[1] It makes use of a generalized Karplus relationship, fits vicinal coupling constant data from NMR spectroscopy to the exocyclic dihedral angles between the coupled protons, and determines the relative populations of each conformer. However, this is not without its problems, as chemically unrealistic conformations are sometimes generated. Here, we make use of an alternative method as a tool to predict $^3J_{H,H}$ values, which can be used for direct comparison to those obtained experimentally. The results of this study, done on a number of alpha-linked arabinofuranosides, were recently reported [2] and will be summarized here.



To extend the above study to beta-arabinofuranosides as these are also present in the mycobacterial cell wall structure, we carried out similar calculations, including Density Functional Theory (DFT) calculations for derivation of Karplus equations that are specifically tailored for these arabinofuranose systems. In addition, molecular dynamics simulations were performed on Methyl beta-D-arabinofuranoside using a variety of forcefields. The results from the various simulations are compared, and an analysis of the resulting $^3J_{H,H}$ values is done. Moreover, access to these J values obtained from the conformational ensemble generated by the MD simulations of these molecules allowed for the direct comparison to ring $^3J_{H,H}$ values obtained from NMR spectroscopy. Such an approach may circumvent possible sources of error entailed by the PSEUROT approach, if not eliminate the need for its use.

[1]. de Leeuw, F.; Altona, C. *J. Comput. Chem.* **1983**, *4*, 428-437.

[2]. Taha, H. A.; Castillo, N.; Sears, D. N.; Wasylshen, R. E.; Lowary, T. L.; Roy, P.J. *Chem. Theory Comput.* **2010**, *6*, 212-222.

Pyramidalization Effects in the Ground-State cis-trans Isomerization of the Green Fluorescent Protein Chromophore

*Qadir Timerghazin*¹, *Alex Brown*² and *Pierre-Nicholas Roy*¹

¹University of Waterloo, Waterloo, ON

²University of Alberta, Edmonton, AB

Green fluorescent protein and its analogues have found widespread use in biology and biochemistry as fluorescent markers. One of the interesting properties demonstrated by some fluorescent proteins is a reversible cis-trans photoisomerization of the chromophore. In many cases, the “dark” trans-form of the chromophore formed as a result of photoisomerization can undergo a spontaneous thermal re-isomerisation back into the fluorescent cis-form. The mechanism of this ground-state cis-trans isomerization is expected to depend both on the intrinsic properties of the chromophore, as well as the on the protein environment. In this contribution, we will discuss hitherto ignored effects of pyramidalization at the carbon atoms involved in the rotation along the C=C bond in the free green fluorescent chromophore molecule based on ab initio calculations and molecular dynamics simulations.

Exploration of Behavior of Pt-Co Core-Shell Nanoparticles Depending on Temperature and Pt-Co Mass Ratio

Andrey Tokarev^{1,2}, Sergey Gusarov², Bock Christina³, Alexander Kobryn² and Andriy Kovalenko^{1,2}

¹Department of Mechanical Engineering, University of Alberta, Edmonton, Alberta, T6G2G8, Canada email: tokarev@uaberta.ca

²National Institute for Nanotechnology, National Research Council of Canada, 11421 Saskatchewan Drive, Edmonton, Alberta, T6G2M9, Canada

³Institute for Chemical Process and Environmental Technology, National Research Council of Canada, Ottawa, Montreal Road Research Facilities 1200 Montreal Road Ottawa, Ontario, K1A 0R6

Core-shell nanoparticles are considered nowadays as promising catalysts for oxidation reduction reaction (ORR) in fuel cells, in particular, PEMFC. One of the main questions of exploitation is their stability.

We perform molecular dynamics (MD) modeling of Pt-Co core-shell nanoparticles using Sutton-Chen potentials [1] with alloy cross-terms [2]. To simulate large nanoparticles of size $> 5\text{nm}$, we use a 'slab model' with periodic boundary conditions and investigate transition processes and final structures as functions of temperature and Pt-Co mass ratio.

We found that a favorable structure of the core-shell nanoparticles is that with platinum atoms located mainly in the surface layer and cobalt atoms in the core. This is in agreement with experimental data and other modeling works [3, 4]. We have found that the final platinum surface concentration increases with Pt-Co mass ratio non-linearly. This concentration influences the catalyst activity of ORR. We also showed that there is a lower temperature limit below which the initial core-shell structure is stable.

[1] A. P. Sutton and J. Chen, *Phil. Mag. Lett.*, 1990, 61, 3, 139.

[2] H. Rafii-Tabar and A. P. Sutton, *Phil. Mag. Lett.*, 1991, 63, 4, 217.

[3] Y. H. Chui and K.-Y. Chan, *Chem. Phys. Lett.*, 2005, 408, 49-53.

[4] V. R. Stamenkovich et al., *Nature*, 2007, v. 6, 241-247.

Rovibrational Energy Levels of Van der Waals Trimers of H₂O and Two Rare Gas Atoms

Xiaogang Wang and Tucker Carrington Jr.

Chemistry Department, Queen's University, Kingston, Ontario, K7L 3N6, Canada

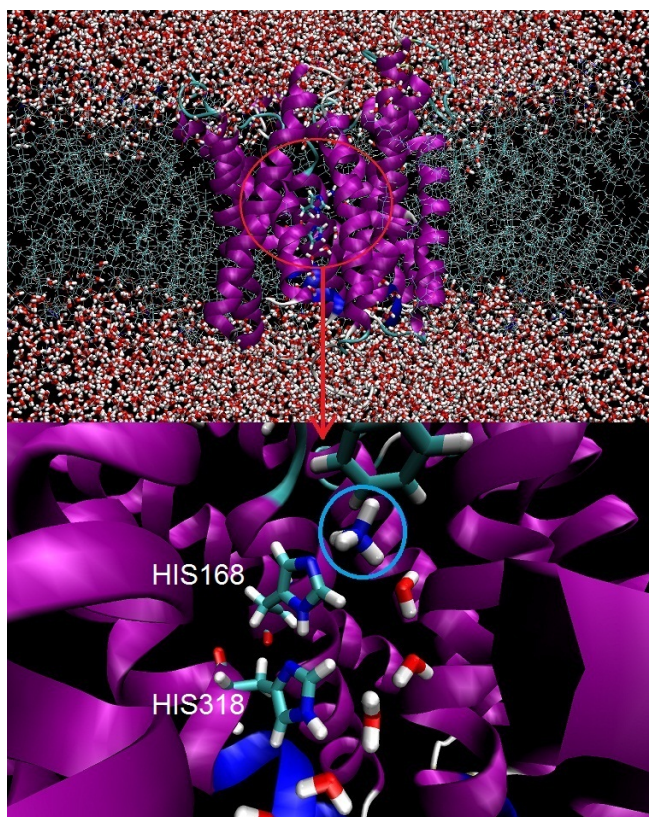
There is a lot of research on linear dopant molecules embedded in helium clusters. The possibility of superfluidity in such clusters has attracted a lot of attention. We propose studying the superfluid and spectroscopic properties of clusters with non-linear dopants such as H₂O. In this poster, as a first step, we discuss the computation of many rovibrational energy levels of several H₂O-Rg₂ Van der Waals trimers, where Rg is a rare gas atom. For these clusters we have identified states with excitation of in-plane and out-of-plane vibrational modes. We focus on two representative systems: H₂O-He₂ and H₂O-Ar₂. For H₂O-He₂, because He atoms are light, calculations are done with orthogonal satellite coordinates. For H₂O-Ar₂, we use (non-orthogonal) satellite coordinates to reduce the potential coupling because Ar is heavy. This increases the complexity of the kinetic energy operator. A new algorithm is devised to deal with this kinetic energy operator. The merits of the two coordinate systems are evaluated for rare gas atoms of different masses.

A Computational Study of the Ammonium Transport in AmtB: Mechanism of NH_3/H^+ Co-Transport

Shihao Wang and Guillaume Lamoureux

Department of Chemistry and Biochemistry, Concordia University, Montréal, QC, H4B 1R6

The transmembrane protein AmtB has an important role in ammonium transport, especially at low external ammonium concentrations. However, whether AmtB is a channel that permeates NH_3 or a transporter that co-transport NH_3 and H^+ is still under debate. In this study, focus is placed on the mechanism of NH_3/H^+ co-transport. An extensive series of QM/MM molecular dynamics simulations has been performed to study the deprotonation mechanism of ammonium. Results of constraint dynamics simulations have been combined to obtain the potentials of mean force for possible deprotonation paths. *Ab initio* calculations have been performed to study the re-protonation of ammonia at the other end of the pore. After the transfer, two residues, His168 and His318, have changed protonation states and need to return to the original states to facilitate the next ammonium transfer. *Ab initio* calculations have been performed to reveal the pathway and energy barrier of this state change.



A snapshot from a simulation of AmtB. In the upper panel, an AmtB monomer is in the center, surrounded by lipids and water. The transport pore is zoomed in and shown in the lower panel, where ammonium is highlighted in a circle and two histidine residues (HIS168 and HIS318) are labelled.

B39

Determination of Molecular Vibrational States using the Ab initio Semiclassical Initial Value Representation

Stephanie Y. Y. Wong¹, Alex Brown¹ and Pierre-Nicholas Roy²

¹Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2

²Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1

The determination of molecular vibrational states quantum-mechanically can be computationally challenging. As one approaches 10s-100s atoms, a semiclassical method is preferable. The Semiclassical Initial-Value Representation (SC-IVR) is a method for calculating the quantum-mechanical time-propagator using classical molecular dynamics trajectories. We have shown that the resultant eigenstates do capture some of the quantum nature of the system. We present the vibrational state results for H₂CO, which serves as a proof-of-principle system for our method. We will describe two implementations of SC-IVR. First, we show our results using full phase space averaging (“standard” SC-IVR) and second, we present similar results using single-trajectory time-averaged SC-IVR (TA-SC-IVR).

B40

Quantum Gate Operations using Mid-Infrared Binary Shaped Pulses on the Rovibrational States of Carbon Monoxide

Ryan Zaari and Alex Brown

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

Frequency domain shaped binary laser pulses were optimized to perform 2-qubit quantum gate operations in ¹²C¹⁶O. The qubit rovibrational state representation was chosen so that all gate operations consisted of 1-photon transitions. The current choice of qubit representation produces pulses with decreased energies and superior fidelities when compared to rovibrational qubit representations consisting of 2-photon transitions. The amplitude and phase varied binary pulses were determined using a Genetic Algorithm optimization routine. Binary pulses have two possible amplitudes, 0 or 1, and two phases, 0 or π , for each frequency component of the pulse. Binary pulses are the simplest to shape experimentally and provide a minimum limit for the fidelity using amplitude and phase shaped pulses. With the current choice of qubit representation and using optimized binary pulses, fidelities of 80% and as high as 97% were achieved for the CNOT and ACNOT quantum gates. This indicates that with a judicious choice of qubits, most of the required control can be obtained with a binary pulse. Limited control was observed for 2-qubit NOT and Hadamard gates due to the need to control multiple excitations. Other diatomic systems besides CO may provide improved fidelities for the 2-qubit NOT and Hadamard quantum gates.

Computational Study of Electronic Structure and Transport in Molecular Junctions

Oleksandr Zelyak¹, Stanislav R. Stoyanov², Sergey Gusarov², Adam Johan Bergren^{2,3},
Richard L. McCreery^{2,3} and Andriy Kovalenko^{1,2}

¹Department of Mechanical Engineering, University of Alberta, Edmonton, AB, Canada,
zelyak@ualberta.ca

²National Institute for Nanotechnology, National Research Council, Edmonton, AB,
Canada, Andriy.Kovalenko@nrc-cnrc.gc.ca

³Department of Chemistry, University of Alberta, Edmonton, AB, Canada

Microelectronic industry has entered the nanoscale regime and is heading toward molecular electronic devices. The latter requires solving fundamental issues of fabricating stable elements, in particular, junctions. We study the large-area molecular junctions fabricated by covalent bonding of aromatic molecular layers to electrodes.

We employ density functional theory and periodic boundary conditions to model infinite length molecular wires and molecular junctions to understand the effects of the molecular architecture on the transport properties.

We focus on calculation of complex band structure and effective electron mass for the infinite molecular chains of phenyl and azobenzene molecules as well as molecular junctions containing phenyl and azobenzene oligomers. These methods should be useful for the rational design of molecular electronic devices.

This work is a part of a collaboration on the development of manufacturable large-area molecular junctions, and is funded in part by the National Research Council.

Model Core Potentials of p-Block Elements Generated Considering the Douglas-Kroll Relativistic Effects, Suitable for Accurate Spin-Orbit Coupling Calculations

Tao Zeng¹, Dmitri G. Fedorov² and Mariusz Klobukowski¹

¹Department of Chemistry, University of Alberta, Edmonton, AB, Canada, T6G 2G2

²RICS, National Institute of Advanced Industrial Science and Technology (AIST), Central 2, Umezono 1-1-1, Tsukuba, 305-8568, Japan

Model core potentials with scalar-relativistic effect at the third order Douglas-Kroll level combined with the first-order Douglas-Kroll for spin-orbit coupling are developed for the 25 p-block elements, B-Tl, with the valence space starting at (n-1)p(n-1)d, except Group 13 where (n-1)s is also included because its importance was clearly demonstrated for Tl. All of the comparisons between model core potential and all-electron calculations of atomic and ionic term and level energies and the spectroscopic constants of monohydrides and cationic dimers indicate the chemical accuracy of our new potentials in reproducing all-electron properties. The timing study demonstrates the extent of the computational savings. We use the recently developed technique of dynamically weighted-MCSCF to generate orbitals for the subsequent spin-orbit coupling calculations, which we call SOC/DW-MCSCF calculations, and studied how the different orbital generation schemes influence the spin-orbit coupling potential energy curves. Our results indicate that using state-specific MCSCF orbitals may lead to discontinuities for potential energy curves when avoided crossing of the electronic states occur and this problem can be solved using state-averaged or dynamically weighted MCSCF orbitals, both of which are found to give similar results when the dynamic electron correlation is considered. The new potentials are applied to cations of homonuclear dimers to establish that polyatomic calculations with MCP atoms are accurate. We clearly show why the earlier MCP-TZP potentials are incapable of producing accurate spin-orbit coupling, especially for the heavier elements, despite the fact the MCP is generally believed to automatically provide accurate radial functions in the core region. The spectroscopic constants of monohydrides of Group 14 elements are calculated as a demonstration of the new family of MCPs extending over all p-elements, which we call ZFK-DK3, and our results compare well with experiment. The CR-CC(2,3) coupled-cluster method was employed to treat the dynamic correlation and correct the underestimated dissociation energies from the MCQDPT calculations. The periodic trends in the spectroscopic properties of cationic dimers and hydrides are discussed.

A Magnetic and Electronic Circular Dichroism Study of Blue Copper Proteins Based on Time-Dependent Density Functional Theory Calculations.

Hristina Zhekova, Michael Seth and Tom Ziegler

Department of Chemistry, University of Calgary, 2500 University Dr. NW, Calgary, Alberta, Canada T2N1N4

Copper proteins have an important role in the living organisms as electron transfer agents or catalytic units involved in oxidation and reduction reactions of immense biological significance. The present study concentrates on the blue copper active sites, which are mononuclear (i.e. have only one copper atom) and participate in rapid inter and intramolecular electron transfer.

Models of four blue copper proteins (azurin, plastocyanin, cucumber basic protein, and nitrite reductase) have been used for theoretical studies of excitation, electronic circular dichroism (CD), magnetic circular dichroism (MCD) and electron paramagnetic resonance (EPR) spectra on the TDDFT/BP86 level. MCD is a technique which measures the differential absorption of right and left circularly polarized light in the presence of external magnetic field. It has been used extensively as a supplement to conventional absorption spectroscopy to probe paramagnetic species like the oxidated copper active sites. However, the analysis of the MCD spectra has been hampered due to the lack of computational methods for the evaluation of the MCD spectroscopic parameters.

A newly developed method is applied here for the theoretical description of the MCD parameters of the aforementioned blue copper models. The calculations reproduce most of the qualitative trends of the observed experimental excitation, CD, MCD, and EPR spectra with some discrepancies in the orbital decompositions and the values of the excitation energies, the $g_{||}$ components of the g tensor, and the components of the A tensor. These discrepancies are discussed relative to deficiencies in the TDDFT methodology and poor performance of the BP86 functional. In addition, the correlation between the MCD and EPR signals has been explored.

Fragments in Molecules. A New Charge and Energy Decomposition Scheme

*Tom Ziegler*¹, *Mariusz P. Mitoraj*² and *Artur Michalak*²

¹Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N1N4

²Department of Theoretical Chemistry, Jagiellonian University, Cracow 30-060, Poland

We have introduced a new scheme for chemical bond analysis by combining the Extended Transition State (ETS) method [*Theor. Chim. Acta* 1977, **46**, 1] with the Natural Orbitals for Chemical Valence (NOCV) theory [*J. Phys. Chem. A* 2008, **112**, 1933]. The ETS-NOCV charge and energy decomposition scheme [*J. Chem. Theory. Comput.* 2009, **5**, 962] makes it not only possible to decompose the deformation density, $\Delta\rho$, into different components (such as σ , π , δ etc.) of the chemical bond, but it also provides the corresponding energy contributions to the total bond energy. Thus, the ETS-NOCV scheme offers a compact, qualitative and quantitative, picture of chemical bond formation within one common theoretical framework. Although, the ETS-NOCV approach contains a certain arbitrariness in the definition of the molecular subsystems that constitute the whole molecule, it can be widely used for the description of different types of chemical bonds. The applicability of the ETS-NOCV scheme will be demonstrated for single ($\text{H}_3\text{X-XH}_3$, for $\text{X} = \text{C, Si, Ge, Sn}$) and multiple ($\text{H}_2\text{X=XH}_2$, H_3CXXCH_3 , for $\text{X} = \text{C, Ge}$) covalent bonds between main group elements, for sextuple and quadruple bonds between metal centers (Cr_2 , Mo_2 , W_2 , $[\text{Cl}_4\text{CrCrCl}_4]^{4-}$) and finally for double bonds between a metal and a main group element ($(\text{CO})_5\text{Cr=XH}_2$, for $\text{X} = \text{C, Si, Ge, Sn}$). Applications are also given to hydrogen- and agostic bonds.

List of Participants

Amgad Albohy
Alberta Ingenuity Centre for
Carbohydrate Science
Department of Chemistry
University of Alberta
albohy@ualberta.ca

Wesley Allen
Department of Chemistry
University of Georgia
wdallen@uga.edu

Alán Aspuru-Guzik
Department of Chemistry and
Chemical Biology
Harvard University
alan@aspuru.com

Cletus Asuquo
Department of Chemistry
University of Saskatchewan
cla121@mail.usask.ca

Khaled Barakat
Department of Physics
University of Alberta
kbarakat@ualberta.ca

Marie Barnes
Department of Chemistry
University of Alberta
mbarnes1@ualberta.ca

Eric Beaudoin
Department of Chemistry
University of Calgary
ebeaudoi@ucalgary.ca

Debasmita Biswal
Department of Chemistry
University of Calgary
dbiswal@ucalgary.ca

Shamus Blair
Department of Chemistry
University of New Brunswick
k8qv4@unb.ca

Russell Boyd
Department of Chemistry
Dalhousie University
russell.boyd@dal.ca

Timm Bredtmann
Institut für Chemie und
Biochemie
Freie Universität Berlin
bredt@chemie.fu-berlin.de

Alex Brown
Department of Chemistry
University of Alberta
alex.brown@ualberta.ca

Satya Bulusu
Department of Chemistry
York University
sbulusu@yorku.ca

Tucker Carrington
Department of Chemistry
Queen's University
tucker.carrington@queensu.ca

Christopher Chapman
Department of Chemistry
University of Victoria
chapmanc@uvic.ca

Hyeonho Choi
Department of Chemistry
Seoul National University
hyeonho.choi@gmail.com

Cassandra Churchill
Department of Chemistry and
Biochemistry
University of Lethbridge
cassandra.churchill@uleth.ca

Edelsys Codorniu-Hernandez
Department of Chemistry
University of Calgary
codorniu@ucalgary.ca

Javier Cuervo
Institute for Biocomplexity and
Informatics
University of Calgary
jcuervo@ucalgary.ca

John Cullen
Department of Chemistry
University of Manitoba
cullen@cc.umanitoba.ca

Gino DiLabio
National Institute for
Nanotechnology
National Research Council of
Canada
Gino.DiLabio@nrc.ca

Harro Dittmar
Department of Chemistry
University of Calgary
hrdittma@ucalgary.ca

Lyudmyla Dorosh
NINT, Department of
Mechanical Engineering
University of Alberta
dorosh@ualberta.ca

Michel Dupuis
Pacific Northwest National
Laboratory
michel.dupuis@pnl.gov

Pavel Elkind
Department of Chemistry
University of Western Ontario
elkindpaul@gmail.com

Matthias Ernzerhof
Department of Chemistry
University of Montreal
matthias.ernzerhof@umontreal.ca

Bryan Faucher
Department of Chemistry
University of Alberta
bfaucher@ualberta.ca

Sarah Fegan
Department of Chemistry
University of British Columbia
skfegan@chem.ubc.ca

Martin Field
Institut de Biologie Structurale
martin.field@ibs.fr

Amelia Fitzsimmons
Department of Chemistry
University of Alberta
afitzsim@ualberta.ca

Rene Fournier
Department of Chemistry
York University
renef@yorku.ca

Douglas Friesen
Department of Oncology
University of Alberta
defriesen@ualberta.ca

Alex Gaiduk
Department of Chemistry
University of Western Ontario
agaiduk@uwo.ca

Melissa Gajewski
Department of Chemistry
University of Alberta
mmg8@ualberta.ca

Mirza Galib
Department of Chemistry
University of Alberta
mgalib@ualberta.ca

John Goddard
Department of Chemistry
University of Guelph
jgoddard@uoguelph.ca

Gabriel Hanna
Department of Chemistry
University of Alberta
gabriel.hanna@ualberta.ca

Haleh Hashemi Haeri
Saarlandes University
Klinikum
hashemihaeri@gmail.com

John Herbert
Department of Chemistry
Ohio State University
herbert@chemistry.ohio-state.edu

Kimihiko Hirao
RIKEN
hirao@riken.jp

Paula Homem-de-Mello
ABCSim
Federal University of
ABC Region
paula.mello@ufabc.edu.br

James Hooper
Department of Chemistry
University of Ottawa
jhoop018@uottawa.ca

Lee Huntington
Department of Chemistry
University of Waterloo
lmhunting@uwaterloo.ca

Radu Iftimie
Department of Chemistry
University of Montreal
radu.ion.iftimie@umontreal.ca

Christopher Ing
Department of Chemistry
University of Waterloo
ing.chris@gmail.com

Chiaki Ishibashi
Chiba Institute of Technology
s0723025RN@it-chiba.ac.jp

Shahid Islam
Department of Chemistry
University of Waterloo
shahid@uwaterloo.ca

Bilkiss Issack
National Institute for
Nanotechnology
University of Alberta
bissack@ualberta.ca

Yumie Kawasaki
Chiba Institute of Technology
s0723282CB@it-chiba.ac.jp

Sergey Kazachenko
Department of Chemistry
University of New Brunswick
t8509@unb.ca

Saheba Khurana
Department of Chemistry
University of British Columbia
skhurana@chem.ubc.ca

Mariusz Klobukowski
Department of Chemistry
University of Alberta
mariusz.klobukowski@ualberta.ca

Christiane Koch
Institut für Theoretische
Physik
Freie Universität Berlin
ckoch@physik.fu-berlin.de

Olga Kravchenko
Department of Chemistry
University of British Columbia
okrav@chem.ubc.ca

Roman Krems
Department of Chemistry
University of British Columbia
roman.krems@gmail.com

Mykhaylo Krykunov
Department of Chemistry
University of Calgary
mkrykuno@ucalgary.ca

Oliver Kühn
Institute of Physics
University of Rostock
oliver.kuehn@uni-rostock.de

Vibha Kumar
Department of Chemistry
Indian Institute of Technology
Roorkee
meenu4s@rediffmail.com

Peter Kusalik
Department of Chemistry
University of Calgary
peter.kusalik@ucalgary.ca

Guillaume Lamoureux
Department of Chemistry and
Biochemistry
Concordia University
glamoure@alcor.concordia.ca

Hui Li
Department of Chemistry
University of Waterloo
huili@uwaterloo.ca

Shuai Liang
Department of Chemistry
University of Calgary
sliang@ucalgary.ca

Ying-Chan Lin
Department of Chemistry
University of Tromsø
ying-chan.lin@uit.no

John Lo
Alberta Sulphur Research Ltd.
jlo@ucalgary.ca

Olga Lyubimova
NINT, Department of
Mechanical Engineering
University of Alberta
olga.lyubimova@ualberta.ca

Chun Chi Mak
CERMM, Department of
Chemistry and Biochemistry
Concordia University
chun@cermm.concordia.ca

Margot Mandy
Program in Chemistry
University of Northern British
Columbia
mandy@unbc.ca

Jonathan Mane
Department of Oncology
University of Alberta
jmane@ualberta.ca

Jiri Mareda
Department of Organic
Chemistry
University of Geneva
jiri.mareda@unige.ch

Alireza Marefatkhah
Department of Chemistry
Shahid Beheshti University
alireza.marefatkhah@gmail.com

Heather Martens
Department of Chemistry
University of the Fraser Valley
heather.wiebe@ufv.ca

Hidenori Matsuzawa
Chiba Institute of Technology
matuzawa@sun.it-chiba.ac.jp

Robert Mawhinney
Department of Chemistry
Lakehead University
rcm@lakeheadu.ca

Shane McCarthy
Department of Chemistry
University of New Brunswick
shane.mccarthy@unb.ca

Bill Meath
Department of Chemistry
University of Western Ontario
wmeath@uwo.ca

Hans-Dieter Meyer
Physikalisch-Chemisches
Institut
Universität Heidelberg
hans-dieter.meyer@pci.uni-
heidelberg.de

Andrea Millen
Department of Chemistry and
Biochemistry
University of Lethbridge
andrea.millen@uleth.ca

Susanna Monti
Istituto per i Processi Chimico-
Fisici
Consiglio Nazionale delle
Ricerche
s.monti@ipcf.cnr.it

Hirotooshi Mori
Division of Advanced Sciences
Ochanomizu University
mori.hirotooshi@ocha.ac.jp

Irina Paci
Department of Chemistry
University of Victoria
ipaci@uvic.ca

Payman Pirzadeh
Department of Chemistry
University of Calgary
ppirzade@ucalgary.ca

Nick Mosey
Department of Chemistry
Queen's University
nicholas.mosey@chem.queensu.ca

Jeffrey Paci
Department of Chemistry
University of Victoria
jtpaci@uvic.ca

Regis Pomes
Molecular Structure &
Function
Hospital for Sick Children
pomes@sickkids.ca

Hiroshi Nakatsuji
Quantum Chemistry Research
Institute
JST CREST
h.nakatsuji@qcri.or.jp

Serguei Patchkovskii
Stearie Institute for Molecular
Sciences
National Research Council of
Canada
Serguei.Patchkovskii@nrc.ca

Tatiana Popa
Department of Chemistry
University of Victoria
tatianap@uvic.ca

Emmanuel Naziga
Department of Chemistry and
Biochemistry
University of Lethbridge
e.naziga@uleth.ca

Gren Patey
Department of Chemistry
University of British Columbia
patey@chem.ubc.ca

Santo Poulouse
National Institute of
Nanotechnology
University of Alberta
poulouse@ualberta.ca

Lam Thanh Nguyen
Atmospheric, Oceanic, and
Space Sciences
University of Michigan
nguyenlt@umich.edu

Jason Pearson
Department of Chemistry
University of Prince Edward
Island
jpearson@upei.ca

Jennifer Przybylski
Department of Chemistry and
Biochemistry
University of Lethbridge
jennifer.przybylski@uleth.ca

Steven Nielsen
Department of Chemistry
University of Texas at Dallas
steven.nielsen@utdallas.edu

Jeffery Perkins
Department of Chemistry
University of the Fraser Valley
jeffery.perkins@ufv.ca

Mickey Richards
Alberta Ingenuity Centre for
Carbohydrate Science
University of Alberta
mickey.richards@ualberta.ca

Marcel Nooijen
Department of Chemistry
University of Waterloo
nooijen@uwaterloo.ca

Gilles Peslherbe
Department of Chemistry and
Biochemistry
Concordia University
Gilles.Peslherbe@concordia.ca

Willian Rocha
Department of Chemistry
Federal University of
Minas Gerais
heidilein@fundep.ufmg.br

Sergei Noskov
Department of Biological
Sciences
University of Calgary
snoskov@ucalgary.ca

Piotr Piecuch
Department of Chemistry
Michigan State University
piecuch@chemistry.msu.edu

Stuart Rothstein
Department of Chemistry
Brock University
srothste@brocku.ca

Christopher Rowan Department of Chemistry University of Victoria crowan@uvic.ca	Klaus Schulten Theoretical and Computational Biophysics Group Beckman Institute University of Illinois at Urbana- Champaign kschulte@ks.uiuc.edu	Ashlyn Smith Department of Chemistry Lakehead University afield@lakeheadu.ca
Pierre-Nicholas Roy Department of Chemistry University of Waterloo pnroy@uwaterloo.ca	Michael Schuurman Steacie Institute for Molecular Sciences National Research Council of Canada Michael.Schuurman@nrc.ca	Jacob Spooner Department of Chemistry University of the Fraser Valley jacob.spooner@ufv.ca
Dmitri Rozmanov Department of Chemistry University of Calgary dmitri.rozmanov@ucalgary.ca	Peter Schwerdtfeger New Zealand Institute for Advanced Study Massey University peter.schwerdtfeger@gmail.com	Viktor Staroverov Department of Chemistry University of Western Ontario vstarove@uwo.ca
Lesley Rutledge Department of Chemistry and Biochemistry University of Lethbridge lesley.rutledge@uleth.ca	Michael Seth Department of Chemistry University of Calgary mseth@ucalgary.ca	Maria Stepanova National Institute for Nanotechnology National Research Council of Canada maria.stepanova@nrc- cnrc.gc.ca
Ilya Ryabinkin Department of Chemistry University of Western Ontario iryabink@uwo.ca	Mariya Shadrina CERMM, Department of Chemistry and Biochemistry Concordia University maria@cermm.concordia.ca	James Stewart Stewart Computational Chemistry MrMOPAC@OpenMOPAC.net
Dennis Salahub Department of Chemistry University of Calgary dennis.salahub@ucalgary.ca	Grigory A. Shamov Department of Chemistry University of Manitoba shamov@cc.umanitoba.ca	Jason Stuber Department of Chemistry University of Waterloo stuber@phds.ca
George Schatz Department of Chemistry Northwestern University schatz@chem.northwestern.edu	Jack Simons Department of Chemistry University of Utah simons@chem.utah.edu	Shuai Sun Department of Chemistry University of Alberta ssun5@ualberta.ca
Markus Schroeder Institute of Physical Chemistry University of Heidelberg markus.schroeder@pci.uni- heidelberg.de	Satya Prakash Singh Department of Chemistry Indian Institute of Technology Roorkee satya0983prakash@rediffmail.com	Dage Sundholm Department of Chemistry University of Helsinki sundholm@chem.helsinki.fi
		Hashem Taha Department of Chemistry University of Alberta htaha@ualberta.ca

Mark Thachuk
Department of Chemistry
University of British Columbia
thachuk@chem.ubc.ca

Ajit Thakkar
Department of Chemistry
University of New Brunswick
ajit@unb.ca

Walter Thiel
Max-Planck-Institut für
Kohlenforschung
thiel@kofo.mpg.de

Peter Tieleman
Department of Biological
Sciences
University of Calgary
tieleman@ucalgary.ca

Qadir Timerghazin
Department of Chemistry
University of Waterloo
qadirt@uwaterloo.ca

Andrey Tokarev
NINT, Department of
Mechanical Engineering
University of Alberta
tokarev@ualberta.ca

Jorge Torres
Department of Chemistry
University of Calgary
jalitorr@ucalgary.ca

Shihao Wang
Department of Chemistry and
Biochemistry
Concordia University
shihaow@gmail.com

Xi Wang
Department of Chemistry
University of Alberta
xw11@ualberta.ca

Yan Alexander Wang
Department of Chemistry
University of British Columbia
yawang@chem.ubc.ca

Xiaogang Wang
Department of Chemistry
Queen's University
xiaogang.wang@umontreal.ca

Noham Weinberg
Department of Chemistry
University of the Fraser Valley
noham.weinberg@ufv.ca

Hans-Joachim Werner
Institute for Theoretical
Chemistry
University of Stuttgart
werner@theochem.uni-
stuttgart.de

Stephanie Wong
Department of Chemistry
University of Alberta
syw@ualberta.ca

Tom Woo
Department of Chemistry
University of Ottawa
twoo@uottawa.ca

Koichi Yamashita
Department of Chemical
System Engineering
University of Tokyo
yamasita@chemsys.t.u-
tokyo.ac.jp

Ryan Zaari
Department of Chemistry
University of Alberta
rzaari@ualberta.ca

Oleksandr Zelyak
NINT, Department of
Mechanical Engineering
University of Alberta
zelyak@ualberta.ca

Tao Zeng
Department of Chemistry
University of Alberta
tzeng@ualberta.ca

Hristina Zhekova
Department of Chemistry
University of Calgary
hzhekova@ucalgary.ca

Rui Zheng
Alberta Ingenuity Centre for
Carbohydrate Science
Department of Chemistry
University of Calgary
zhar@ucalgary.ca

Baojing Zhou
Department of Chemistry
University of Calgary
bzho@ucalgary.ca

Tom Ziegler
Department of Chemistry
University of Calgary
ziegler@ucalgary.ca

Abstracts Author Index

- Akhvlediani, R., 97
Albohy, Amgad, 44
Ali-Torres, Jorge, 45
Allen, Wesley, 12
Andrae, D., 50
Aspuru-Guzik, Alán, 40
Asuquo, Cletus, 45
- Baoukina, Svetlana, 19
Barakat, Khaled, 46, 62
Barker, J. R., 96
Barone, Vincenzo, 93, 94
Barth, I., 50
Beaudoin, Eric, 47, 99
Bennett, Drew, 19
Bergren, Adam Johan, 124
Berjanskii, Mark, 58, 72, 101
Biswal, Debasmita, 48
Blair, Shamus A., 49
Blinov, Nikolay, 58
Boese, A. Daniel, 55
Boese, Roland, 55
Boguslavskiy, Andrey, 109
Boon, Nicholas, 87
Bowles, Richard K., 45
Boyd, Russell, 38
Bredtmann, Timm, 50
Brown, Alex, 56, 119, 123
Budzelaar, Peter H. M., 112
Bulusu, Satya, 51, 61
- Cacelli, Ivo, 93, 94
Cairo, Christopher W. , 44
Cardoso, Daniel R., 65
Carrington Jr., Tucker, 121
Chapman, Chris, 15, 52
Choi, Hyeonho, 53
Christina, Bock, 120
Churchill, Cassandra D.M., 54
Clark, Peter, 80
Codorniu-Hernandez, Edelsys, 55
Cuervo, Javier E., 56
- Da Silva, Julio, 104
Dance, Paul, 25, 87
Deglint, Elna, 87
Dittmar, Harro, 57
Dorosh, Lyudmyla, 58
Dupuis, Michel, 14
Dyck, Greg, 98
- Edwards, Essex, 25, 87, 98
Elkind, Pavel D., 59
Emery, Daniel, 86
English, Ann, 111
Ensing, Bernd, 29
Ernzerhof, Matthias, 59
- Fedorov, Dmitri G., 125
Fegan, Sarah K., 60
Fenske, Bruce, 62
Ferretti, Alessandro, 93, 94
Field, Martin, 20
Fitzsimmons, Amelia, 60
Fournier, Rene, 51, 61
Friesen, Douglas, 62
- Gaiduk, Alex P., 62
Gajewski, Melissa, 63
Garde, Shekhar, 18
Gatti, Fabien, 27
Geva, Eitan, 23
Gouzman, Irina, 97
Grossman, Eitan, 97
Gusarov, Sergey, 81, 120, 124
- Hanna, Gabriel, 23
Hashemi Haeri, Haleh, 64
Hege, H.-Ch., 50
Herbert, John, 39
Herrera, Felipe, 31
Hinsen, Konrad, 69
Hirao, Kimihiko, 33
Hoffman, Alon, 97
Homem-de-Mello, Paula, 65
Hooper, James, 66

Hoth, Markus, 64
 Huber, Liam, 25
 Huntington, Lee M.J., 67

 Iftimie, Radu, 68
 Ing, Christopher, 69
 Ishibashi, Chiaki, 70
 Islam, Shahid, 71
 Issack, Bilkiss, 46, 72
 Iwata, Suehiro, 73

 Jacobson, Leif, 39
 Jager, Wolfgang, 78

 Kühn, Oliver, 26
 Kamstra, Rhiannon, 90
 Kappl, Reinhard, 64
 Kawasaki, Yumie, 73
 Kazachenko, Sergey, 74
 Khurana, Saheba, 75
 Klobukowski, Mariusz, 60, 63, 125
 Knippers, David, 57
 Kniza, Gerald, 13
 Kobryn, Alexander, 81, 120
 Koch, Christiane, 30
 Koch, Denise, 82, 111
 Kovalenko, Andriy, 58, 81, 120, 124
 Kravchenko, Olga, 75
 Krems, Roman, 31
 Krykunov, Mykhaylo, 76
 Kumar, Vibha, 77
 Kusalik, Peter, 47, 48, 57, 79, 99, 106

 Lamoureux, Guillaume, 22, 122
 Le Roy, Robert J. , 78
 Lev, Bogdan, 17
 Li, Hui, 78
 Li, Matthew, 44
 Li, Wei, 11
 Liang, Shuai, 79
 Litinskaya, Marina, 31
 Liu, Xiangjun, 81
 Lo, John, 80
 Losilla, Sergio A., 117
 Lowary, Todd, 71, 103, 118
 Lyubimova, Olga, 81

 Mak, Chun C., 82, 83
 Manderville, Richard A., 92
 Mandy, Margot, 84
 Mane, Jonathan, 62, 85
 Manz, J., 50
 Mareda, Jiri, 86
 Marquardt, F., 50
 Martens, Heather, 87
 Matile, Stefan, 86
 Matsuzawa, Hidenori, 70, 73, 88
 Maurer, Patrick, 68
 Mawhinney, Robert, 89, 90, 114
 McCarthy, Shane P., 91
 McCreery, Richard L., 124
 McKellar, A. R. W., 78
 Meyer, Hans-Dieter, 27
 Michalak, Artur, 127
 Midorikawa, Makoto, 88
 Millen, Andrea L., 92
 Minton, Timothy, 97
 Mitoraj, Mariusz P. , 127
 Miyoshi, Eisaku, 60
 Montero-Cabrera, Luis Alberto, 55
 Monti, Susanna, 93, 94
 Moore , Preston B., 29
 Mori, Hirotooshi, 43, 60
 Mosey, Nicholas, 34

 Nakatsuji, Hiroshi, 41
 Naziga, Emmanuel B., 95
 Nguyen, T. L., 96
 Nielsen, Steven O., 29
 Nooijen, Marcel, 67, 116
 Noskov, Sergei, 17

 Oblinsky, Daniel G., 32
 Ohtsuki, Yukiyoshi, 53

 Paci, Irina, 15, 52, 100, 105
 Paci, Jeffrey, 97
 Patchkovskii, Serguei, 98
 Paulus, B., 50
 Pearson, Jason, 37
 Perez-Rios, Jesus, 31
 Perkins, Jeffery, 25, 98
 Peshherbe, Gilles, 82, 83, 111

Piecuch, Piotr, 11
 Pirzadeh, Payman, 47, 99
 Popa, Tatiana, 15, 100
 Poulouse, Santo, 101
 Prachnau, Melissa , 25
 Prampolini, Giacomo, 93, 94
 Proud, Adam, 37
 Przybylski, Jennifer L., 102

 Raston, Paul L., 78
 Rauk, Arvi, 45
 Richards, Mickey, 103
 Rocha, Willian, 104
 Rodriguez-Rosario, Cesar, 40
 Rolo-Naranjo, Alberto, 55
 Rothstein, Stuart, 32
 Rowan, Christopher, 105
 Roy, Pierre-Nicholas, 69, 71, 78, 118, 119, 123
 Rozmanov, Dmitri, 106
 Rutledge, Lesley, 107
 Ryabinkin, Ilya G., 36, 108

 Schatz, George, 16, 97
 Schauerte, Carsten, 55
 Schreckenbach, Georg, 112
 Schroeder , Markus, 27
 Schulten, Klaus, 24
 Schuurman, Michael, 109
 Schweizer, Frank, 95
 Schwerdtfeger, Peter, 42
 Seth, Michael, 110, 126
 Shadrina, Mariya, 111
 Shamasundar, K.R., 13
 Shamov, Grigory A., 112
 Shen, L., 97
 Shin, Seokmin, 53
 Shiozaki, Toru, 13
 Shizgal, Bernie, 75
 Shpilman, Ze'ev, 97
 Simons, Jack, 9
 Singh, Satya Prakash, 113
 Smith, Ashlyn, 114
 Song, Jong-Won, 33
 Spannel, Michael, 98
 Spooner, Jacob, 115

 Stanton, J. F., 96
 Staroverov, Viktor N., 36, 59, 62, 108
 Stepanova, Maria, 46, 72, 101
 Stewart, James, 10
 Stolow, Albert, 109
 Stoyanov, Stanislav R., 124
 Stuber, Jason, 116
 Sundholm, Dage, 117
 Suzuki, Satoshi, 33

 Taha, Hashem, 118
 Tempel, David, 40
 Thachuk, Mark, 60, 75
 Thakkar, Ajit J., 49, 74, 91
 Thankachan, P.P., 77, 113
 Thiel, Walter, 21
 Thomas, Vibin, 68
 Tieleman, Peter, 19
 Timerghazin, Qadir, 83, 119
 Tokarev, Andrey, 120
 Tseng, Chih-Yuan, 62
 Tsuneda, Takao, 33
 Tuszynski, Jack, 46, 62, 63, 85

 Vendrell, Oriol, 27

 Wang, Shihao, 22, 122
 Wang, Xiaogang, 121
 Weinberg, Noham, 25, 87, 98, 115
 Werner, Hans-Joachim, 13
 Wetmore, Stacey, 54, 92, 95, 102, 107
 Wishart, David, 58, 72, 101
 Wolfe, Saul, 115
 Wong, Stephanie Y. Y., 123
 Woo, Tom, 35, 66

 Yamashita, Koichi, 28
 Yan, Yun-an, 26
 Yuen, Wai Kong, 32
 Yuen-Zhou, Joel, 40

 Zaari, Ryan, 123
 Zelyak, Oleksandr, 124
 Zeng, Tao, 125
 Zhekova, Hristina, 126
 Zheng, Ruixiang Blake, 44

Ziegler, Tom, 76, 80, 110, 126, 127

Zou, Chunxia, 44

Zou, Yao, 44