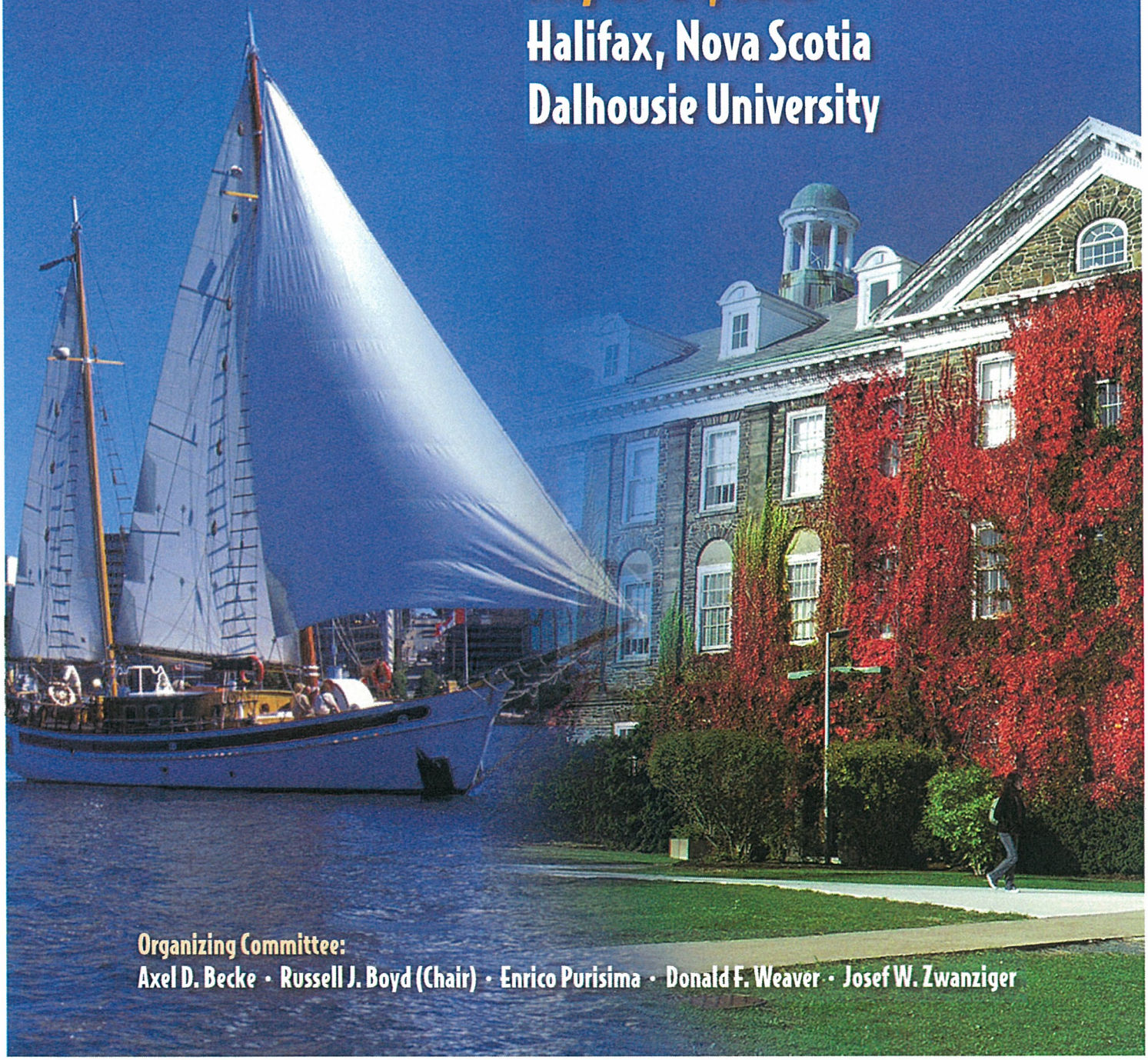
7th Canadian Computational Chemistry Conference

July 20-24, 2009

Halifax, Nova Scotia

Dalhousie University



Organizing Committee:

Axel D. Becke · Russell J. Boyd (Chair) · Enrico Purisima · Donald F. Weaver · Josef W. Zwanziger

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Dalhousie University
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Internet Access

Guest accounts for internet access will be provided at the Registration Desk. Internet access will be available in the McCain Building and several other locations on campus. Computers for internet access will be available in the Killam Library, which is on the opposite side of LeMarchant Street from the McCain Building.

Welcome

As the organizers of the 7th Canadian Computational Chemistry Conference (CCCC7), it is a pleasure to welcome you to Halifax, the capital of Nova Scotia, and to Dalhousie University, the largest university in the Maritime Provinces. We extend a warm welcome to our many international participants from more than 20 countries.

The CCCC is a triennial celebration of excellence in all branches of computational chemistry. The tradition began in 1991 and has continued as follows:

Orford, Quebec, 1991
Kingston, Ontario, 1994
Edmonton, Alberta, 1997
Lennoxville, Quebec, 2000
Toronto, Ontario, 2003
Vancouver, British Columbia, 2006

The CCCC7 technical program consists of 37 invited lectures by leaders in many branches of computational chemistry and about 100 poster presentations divided into two sessions. Collectively, the oral and poster presentations will offer all participants an opportunity to learn about the latest developments in computational chemistry and to discuss the opportunities for new directions and applications.

We hope that you will take some time to experience some of the highlights of Halifax and Nova Scotia. Recommended attractions close to Dalhousie University include the Public Gardens, the Halifax Citadel, the Maritime Museum of the Atlantic, and Pier 21, Canada's National Museum of Immigration.

We are delighted to acknowledge the generous support of our sponsors who are listed on the following page.

Welcome to Nova Scotia, welcome to Halifax, and welcome to the 7th Canadian Computational Chemistry Conference.

Axel D. Becke (Dalhousie University)
Russell J. Boyd (Dalhousie University)
Enrico O. Purisima (NRC Biotechnology Research Institute)
Donald F. Weaver (Dalhousie University)
Josef W. Zwanziger (Dalhousie University)

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CRC Press Award for Excellence in Computational Chemistry

At the CCCC6 in 2006, Taylor & Francis/CRC Press introduced a book award, the *CRC Press Award for Excellence in Computational Chemistry*, for posters presented by students and postdoctoral fellows. Two awards will be made at the CCCC7. Each awardee will receive a certificate and a copy of the latest edition of the CRC Handbook of Chemistry and Physics.

Daily Program

Monday, July 20		
4:00	Registration in the foyer of the McCain Building	
7:00	Opening reception in the foyer and courtyard of the McCain Building	
Tuesday, July 21		
8:55	Official opening	
	Session Chair: Andre Bandrauk	
9:00	**Martin Head-Gordon**	Chemicurrent from oxidative chemical reactions on metal surfaces: Modeling fast electron generation.
9:40	**Rod Bartlett**	Do We Really Need DFT? Alternative Correlated Orbital Theories From Wavefunction Theory
10:20	Coffee break	
	Session Chair: Nelaine Mora-Diez	
10:40	**Laura Gordon**	Restricted active space second order perturbation theory (RASPT2) versus CASPT2 for the treatment of non-dynamical electron correlation
11:20	**Mark Gordon**	Fragmentation Methods: Accurate Calculations For Large Molecular Systems
12:00	**Peter Pulay**	Efficient Atomic Simulation of Solvent Effects
12:40	Lunch break	
	Session Chair: Ray Poirier	
2:00	**Emily A. Carter**	Linear Scaling Quantum Mechanics Methods for Molecules and Materials
2:40	**David Vanderbilt**	Orbital magnetization and magnetoelectric phenomena in solids
3:20	Coffee break	
	Session Chair: Jesus Ugalde	
3:40	**Michele Parrinello**	Coloring the noise
4:20	**Mark Tuckerman**	Solvation and transport of charged topological defects in water, vacuum/water interfaces, and other hydrogen-bonded media.
6:00	Harbour cruise	
Wednesday, July 22		
	Session Chair: Mark Thachuk	
9:00	**Marina Guenza**	Analytical coarse-grained theories to bridge timescales in the dynamics of macromolecular systems
9:40	**Raymond Kapral**	Moving in a Crowded World
10:20	Coffee break	
	Session Chair: Tony Ford	
10:40	**David Clary**	Combining quantum dynamics and quantum chemistry for reactions of polyatomic molecules
11:20	**Sharon Hammes-Schiffer**	Nuclear-Electronic Orbital Approach: Electron-Proton Correlation and Multicomponent Density Functional Theory
12:00	**Tucker Carrington**	New strategies for solving the vibrational Schrödinger equation
12:40	Lunch break	
	Session Chair: Janet Del Bene	
2:00	**Krishnan Raghavachari**	QM/QM Electronic Embedding Models for Materials Chemistry
2:40	**Berny Schlegel**	Exploring Potential Energy Surfaces Using Ab Initio Molecular Dynamics
3:20	Coffee break	
	Session Chair: Stacey Wetmore	

3:40	**Leo Radom**	The Role of Radicals in Coenzyme-B_{12}-Mediated Reactions: A Computational Approach
4:20	**Pavel Hobza**	Accurate Interaction Energies of Building Blocks of Biomacromolecules and the Role of Dispersion Energy
	Session Chair: Jaime Martell	
5:00	Poster session in the McInnes Room	
	Thursday, July 23	
8:30	Business meeting to choose organizers of the CCCC in 2012	
Morning sessions sponsored by: Chemical Computing Group		
	Session Chair: Heather Gordon	
9:00	**Christopher Bayly**	A Neo-Classical EPIC on Electronic Polarization for Biomolecular Simulations
9:40	**Arvi Rauk**	Alzheimer's Disease - Chemical Causes and Prevention
10:20	Coffee break	
	Session Chair: John Goddard	
10:40	**Jiali Gao**	X-Pol Potential: From Lifson Molecular Mechanics to Quantal Force Field for Biomolecular Simulations
11:20	**William L. Jorgensen**	Progress and Challenges in Modeling Organic and Biomolecular Systems
12:00	**Dennis Salahub**	Towards the multiscale modeling of biological systems and processes – progress on RNA polymerase and transcription
12:40	Lunch break	
	Chair: Viktor Staroverov	
2:00	**Weitao Yang**	Insights and Progress in Density Functional Theory.
2:40	**John P. Perdew**	Workhorse Semilocal Density Functional for Condensed Matter Physics and Quantum Chemistry
3:20	Coffee break	
	Chair: Jim Wright	
3:40	**Gustavo Scuseria**	New models for mixing wavefunctions with density functional theory
4:20	**Matthias Ernzerhof**	Electrons passing through molecules
	Session Chair: Jason Pearson	
5:00	Poster session in the McInnes Room	
7:30	Lobster dinner in the Great Hall	
	Friday, July 24	
	Session Chair: Natalie Cann	
9:00	**Ajit Thakkar**	TIP4P, TTM2.1-F and AMOEBA water clusters: Evolution of properties of the global minima with size
9:40	**Tom Ziegler**	Reinterpreting the Determinantal Ansatz in Kohn-Sham Theory. New Variational Approaches to Excited and (Nearly) Degenerate States in Density Functional Theory.
10:20	Coffee break	
	Session Chair: James Gauld	
10:40	**Peter Gill**	Approaching the Hartree-Fock limit by perturbative methods
11:20	**David Mazziotti**	Two-electron Reduced-Density-Matrix Mechanics: With Application to Many-electron Atoms and Molecules
12:00	**Paul Ayers**	Variational Reduced Density Matrix Theory: Successes and Failures
12:40	Lunch break	
	Session Chair: Mariusz Klobukowski	
2:00	**Aatto Laaksonen**	Modelling soft, hard and porous materials

2:40	**Natalie Holzwarth**	A Projector Augmented Wave Formulation of the Optimized Effective Potential Formalism[a]
3:20	Coffee break	
	Session Chair: Manuel Yanez	
3:40	**Pierre-Nicholas Roy**	Imaginary and real time quantum dynamics with applications to weakly bound clusters
4:20	**Gren Patey**	Simulation of Ionic Liquids: How Ionic Structure Influences Macroscopic Behaviour
5:00	**Andriy Kovalenko**	Multiscale Theories in Computational Chemistry: From Super CI and DFT for Electronic Structure to 3D Molecular Theory of Solvation and to Hydrodynamic Boundary Conditions
5:40	Closing comments	

Poster Session I, Wednesday afternoon, July 22

No.	*Presenter*	*Title*
[P1-1]	Al-Hashimi, Nessreen	Ab-initio study on the formation of tri-iodide CT complex from the reaction of iodine with n-electron donors
[P1-2]	Ali, Mohamad Akbar	Computational studies on cyclic [n]paraphenyleneacetylenes and cyclic butadiyne-bridge [4n]paracyclophynes using homodesmotic reactions
[P1-3]	Almatarneh, Mansour	Molecular Dynamics Simulations of Protein (HLA-Cw6-B2m-KIR2DS2) Associated with Skin Disease Psoriasis
[P1-4]	Arabi, Alya	Geometrical Similarity of the Disposition of the Electrostatic Potential of Tetrazole and Carboxylic Group at the Root of their Bioisosteric Relationship
[P1-5]	Azriel, Vladimir	Mechanism of ionic recombination in the system $Cs^+ + Br^- + Xe$
[P1-6]	Barakat, Khaled	Ensemble-based virtual screening reveals novel inhibitors for the MDM2-p53 interaction
[P1-7]	Bohorquez, Hugo J	Atomic sizes in terms of physical observables
[P1-8]	Bolesta, Alexey	Molecular dynamics simulation of argon nucleation from supersaturated vapor
[P1-9]	Bryjko, Lilianna	SA-CASSCF and R-matrix calculations of low-energy electron collisions with uracil
[P1-10]	Burke, Luke	Computational Study of the [1,4] Sigmatropic Shift
[P1-11]	Bushnell, Eric	A theoretical investigation on the possible mechanism of UROD
[P1-12]	Campagna-Slater, Valérie	Virtual Screening of the Protein Data Bank: Searching for Sites with Pre-defined Chemistry
[P1-13]	Cann, Natalie	Chirality transfer at chiral stationary phases: Insights from simulations
[P1-14]	Carreon-Macedo, Jose-Luis	Ab-initio potential energy and dipole moment surfaces for CS_2: Towards an optimal control of a CARS process using the OCT-MCTDH approach
[P1-15]	Carvalho, Alexandra	Reverse transcriptase resistance to NRTIs: PPi leaving is coupled to fingers domain opening
[P1-16]	Chan, Anita	Amphiphilic Alternating Copolymer Nanoarchitectures: The Characterization of Poly(Isobutylene-alt-maleic acid)
[P1-17]	Chevrier, Vincent	First Principles Modeling of the Lithiation of Silicon
[P1-18]	Churchill, Cassandra	A Computational Study of Stacking and T-shaped Interactions of the DNA Nucleobases with Protonated or Neutral Histidine
[P1-19]	Constas, Styliani	Molecular simulations of fragmentation processes in nano-clusters in the presence of charged macromolecules.
[P1-20]	Craddock, Travis	Computational Determination of Putative Binding Sites of Anesthetics to the Cytoskeleton
[P1-21]	Cuevas-Saavedra, Rogelio	Alternative Ornstein-Zernike Models for the Homogeneous Electron Liquid
[P1-22]	Cui, Qizhi	QM/MM Simulations and High-throughput Virtual Screening on UDP-Sugar Hydrolases from the Pseudaminic Acid Biosynthetic Pathway
[P1-23]	Cullen, John	Many Body Perturbation Methods Implemented into a Diatomics in Molecules Hamiltonian
[P1-24]	Dharma-wardana, Chandre	The Classical-Map Hyper-Netted-Chain (CHNC) technique for inhomogeneous electron systems- an order-zero method. *Application to quantum dots.*
[P1-25]	Difley, Seth	Electronic Couplings between Charge-transfer States and Excitons in Organic Photovoltaics
[P1-26]	Dourado, Daniel	Glutathione transferase: GSH activation mechanism proposal
[P1-27]	Dunlap, Brett	Perturbation Theory in the Space of Variationally Fitted Kohn-Sham Potentials
[P1-28]	East, Allan	Ab initio Alkyl Ions: Open and Closed (PCP^+) Structures

[P1-29]	East, Allan	Entropy Contributions in pKa Computation: Application to Alkanolamines and Piperazines
[P1-30]	Echegaray, Eleonora	Is the Condensed Fukui Function Negative in Charge Disproportionation Compounds?
[P1-31]	Eizaguirre, Ane	Why do α,β-Unsaturated and Saturated derivatives of Mg and Ca behave as Metal Acids in the Gas Phase?
[P1-32]	Erdtman, Edvin	Elucidation of the mechanism of Porphobilinogene synthase
[P1-33]	Ford, Tony	An Ab Initio Molecular Orbital Study of the Complexes Formed Between Silicon Tetrafluoride and Some Lewis Bases
[P1-34]	Franco, Hector	Gold cluster stability effects on the localized spin density at the possible sites of chemisorption
[P1-35]	Gajewski, Melissa	Structure and properties of peloruside A: Towards understanding of anti-cancer activity
[P1-36]	Ghysels, An	Normal mode calculations with the QM/MM full Hessian and the Mobile Block Hessian (MBH) method
[P1-37]	Gordon, Heather	Self-Organizing Map Analysis of Protein Conformational Distributions: Discrimination between Induced Fit and Conformational Isomerism for an Intrinsically Flexible Binding Site
[P1-38]	Goyer, Francois	Modelling correlation effects in molecular electronics devices
[P1-39]	Groves, Michael	Predicting Proton Exchange Membrane Fuel Cell Platinum Catalyst Durability and Activity using Density Functional Theory
[P1-40]	Gunawan, Rahmat	The Potential Energy Surface for hydrogen on Alkali-Graphite Intercalates: A Density Functional Theory Investigation
[P1-41]	Hepperle, Steven	Computational Studies of $ZnR_2/ZnCl_2$ Reactions with Zincocenes and the Anomalous Formation of Decamethyldizincocene.
[P1-42]	Hernandez-Marin, Elizabeth	DFT study of the oxygen atom transfer reaction between DMSO and the molybdoenzyme DMSO reductase.
[P1-43]	Heverly-Coulson, Gavin	Study of the Antioxidant Potential of Small Selenium-Containing Molecules
[P1-44]	Hollett, Joshua	Electron Correlation I: Theories
[P1-45]	Hollett, Joshua	Electron Correlation II: Properties
[P1-46]	Huang, Wenjuan	The redox glycoside hydrolysis mechanism catalyzed by GlvA: A DFT Study
[P1-47]	Iftimie, Radu	Using a through-space modeling of substituent effects to study the dissociation of moderately strong acids in water by means of first-principles molecular dynamics simulations
[P1-48]	Islam, Shahidul M.	Calculation of arabinanase-ligand binding free energy by computer simulation: the challenge of oligofuranosides
[P1-49]	Issack, Bilkiss	Effect of cholesterol on transport across membranes: a computational investigation
[P1-50]	Jalili, Seifollah	Molecular Dynamics Simulations of Sodium Dodecyl Sulfate Micelles Using a Coarse-Grained Model
[P1-51]	Jensen, Svend Knak	Estimate of acid constants for HCOO(aq) and OH(aq) using electron structure calculations

Poster Session 2, Thursday afternoon, July 23

No.	*Presenter*	*Title*
[P2-1]	Issack, Bilkiss	Quantum Effects in Theoretical Investigations of Water Photolysis: $(H_2O)_2^+$ as a Case Study
[P2-2]	Johnson, Erin	A Quantum-Mechanical Description of the Lennard-Jones Potential between QM/MM Subsystems
[P2-3]	Kannemann, Felix	Application of dispersion-corrected density functional theory to benchmark sets of intermolecular interactions
[P2-4]	Keefe, Dale	Computational Study of Proper and Improper Hydrogen Bonding in Binary Methanol Complexes
[P2-5]	Lamoureux, Guillaume	Exploring proton transfer pathways in the ammonia channel AmtB
[P2-6]	Lamsabhi, Al mokhtar	The Mechanism of Double Proton Transfer in Dimers of Uracil and 2-Thiouracil: The Reaction Force Perspective
[P2-7]	Landau, Arie	Frozen Natural Orbitals for Ionized States within Equation-Of-Motion Coupled-Cluster Formalism
[P2-8]	Llano, Jorge	Oxidative Dealkylation Mechanism by Fe(II)-Dependent AlkB Family of Enzymes: A DFT Study
[P2-9]	Lopez-Tarifa, Pablo	TDDFT molecular dynamics simulations of the fragmentation of ionized biomolecules in gas phase and water environment
[P2-10]	Mandy, Margot	Threshold determination in the dissociation of $H_2(v,j) + H_2(v',j')$
[P2-11]	Mane, Jonathan	Modeling cytotoxic activity of colchicine derivatives in different cancer cell lines
[P2-12]	Mawhinney, Robert	Silicon-29 Shielding Constants and Tensors Via Computational Methods
[P2-13]	Mawhinney, Robert	Five-Coordinate Silicon Complexes with Threitol and Erythritol
[P2-14]	McCarthy, Shane	Highly accurate momentum space pair densities and two-electron properties for the excited states of two-electron systems.
[P2-15]	McNeil, Nicole	Modeling the Ionization of Threonine in the Gas Phase
[P2-16]	Meek, Autumn	Solapsone as a Disease Modifying Drug for Alzheimer's Disease
[P2-17]	Millen, Andrea	Effects of 8-Aryl Substituents on the Structure and Stability of Purine Nucleic Acids
[P2-18]	Mora-Diez, Nelaine	The Baeyer-Villiger Reaction: Ionic or Neutral?
[P2-19]	Mosey, Nick	Extending the Time-Scales Accessible in Molecular Dynamics Simulations of Reactions
[P2-20]	Nassimi, Ali	Quantum-classical dynamics in the mapping basis and its relation to the subsystem basis
[P2-21]	Oblinsky, Daniel	Do point mutations evoke disperse entropic changes throughout a protein domain?
[P2-22]	Orlova, Galina	The Performance of DFT in Prediction of Radical-Cationic Amino Acids
[P2-23]	Pearson, Jason	Can Correlation Bring Electrons Closer Together?
[P2-24]	Przybylski, Jennifer	Modeling the Hydrolysis of DNA Nucleosides
[P2-25]	Puerta, Luis	Approximation Level of Calculation Effects in the Estimation of Intermolecular Electronic Charge Transfer in Lewis Type Acid-Base Adducts
[P2-26]	Purisima, Enrico O.	Refinement of a Continuum Electrostatics-Dispersion Model of Solvation. Prospective Studies and Retrospective Analyses from the SAMPL Challenges.
[P2-27]	Rahimi, Rahmatollah	Theoretical studies on the structural change in the N-protonated Tetra(p-hydroxyphenyl)porphyrin
[P2-28]	Rothstein, Stuart	Polyglutamine Monomer Structure and its Implications for Molecular Self-Assembly
[P2-29]	Rowan, Christopher	Polarization and Permittivity of Nanocomposites through MD and DFT

[P2-30]	Rutledge, Lesley	Noncovalent Interactions at Natural or Damaged DNA Nucleobase-Protein Interfaces
[P2-31]	Safinejad, Feryal	Effect of alkyl chain length on the interaction between phenolic esters and water molecules
[P2-32]	Safinejad, Feryal	Detailed assignment of UV-vis absorption spectra of high spin heme derivatives
[P2-33]	Sameera, W. M. C.	Biomimetic water oxidation: some clues from computational chemistry
[P2-34]	Schweigert, Igor	Symmetry-broken independent-particle models in Born-Oppenheimer molecular dynamics of chemical bond dissociation
[P2-35]	Shamov, Grigory A.	Testing the performance of DFT-D corrections for hydrocarbons: enthalpies of hydrocarbon isomerizations and olefin polymer growth reactions
[P2-36]	Shamov, Grigory A.	Binuclear Uranium(VI) Complexes with a "Pacman" Expanded Porphyrin: a Computational Probe for Unusual Bis-Uranyl Structures
[P2-37]	Sheykhshoaieekhtiarabadi, Saeed	Relationship Between the Electronic Property and the Corrosion Inhibition Activity of Some Organic Compounds
[P2-38]	Staroverov, Viktor	Kohn-Sham Methods with Model Exchange-Correlation Potentials
[P2-39]	Szakacs, Csaba	Electronic structure and doping in ZnO bulk, slabs, and clusters
[P2-40]	Taylor, Alexis	Electronic Nature of a Self-Assembled ADADA Hydrogen-Bonded Helix
[P2-41]	Thachuk, Mark	Towards an understanding of the dissociation mechanism of gas phase protein complexes
[P2-42]	Thomas, Vibin	Towards understanding the dissociation mechanism of a weak acid in aqueous solution
[P2-43]	Timerghazin, Qadir	Ground-State Green Fluorescent Protein Chromophore Z-E isomerization
[P2-44]	Vinogradov, Ivan	Monte Carlo atomic simulations with coordinate transformations.
[P2-45]	Walker, Victoria	The Effect of Multiplicity on the Structure of Iron (II) and Iron (II) Porphyrins
[P2-46]	Whittleton, Sarah	Monofluoridation and Difluoridation: Examing the Thermodynamic Effects of Added Nucleophiles on the Dimerization of Acyclic and Cyclic Dialkyldialkoxystannanes
[P2-47]	Wong, Stephanie	Vibrational states of H_2CO: A direct dynamics semiclassical initial value representation approach
[P2-48]	Wright, James	Improving the safety of estrogen supplements by avoiding carcinogenic pathways
[P2-49]	Wu, Jian	DFT calculation of a polaron in DNA
[P2-50]	Zeng, Tao	Model core potentials for studies of scalar relativistic effects and spin-orbit coupling at Douglas-Kroll level. I. Theory and applications to Pb and Bi
[P2-51]	Zhou, Yongxi	Applications and extensions of the source-sink potential approach
[P2-52]	Ziegler, Tom	Fragments in molecules

Invited Talks

Arranged in presentation order

[O-1]

Chemicurrent from oxidative chemical reactions on metal surfaces: Modeling fast electron generation.

Sergey Maximoff and Martin Head-Gordon
Department of Chemistry, University of California, and,
Chemical Sciences Division, Lawrence Berkeley National Laboratory
Berkeley, CA 94720
USA

Under special experimental conditions, a chemical reaction on a metal surface, specifically the oxidation of CO to CO_2 on Pt, has been experimentally shown to generate electricity as a by-product of the surface chemistry under steady state conditions. The chemicurrent yield is not negligible (nor is it high): roughly one in every 10^3 reaction events produces an electron with more than 1 eV kinetic energy. Furthermore transient chemicurrent has also been seen in the adsorption of diverse species (from rare gas atoms to molecules such as CO and oxygen) onto metal surfaces. The transient chemicurrent yield for adsorption exhibits power law scaling with heat of adsorption.

These two sets of data raise very interesting questions that at present are difficult to address experimentally. What is special about CO oxidation on Pt that causes chemicurrent? What is the molecular origin of chemicurrent generation in this system? What controls chemicurrent yield? What is the origin of power law scaling? In this talk, the experimental results will be reviewed, and then a phenomenological framework for chemicurrent generation[1] will be described. Its application to the CO oxidation reaction will be presented, based on electronic structure calculations. The application of the same methodology to catalytic hydrogen oxidation (to water) for which experimental results have just been obtained will also be described. Finally, the origin of the power law scaling seen in the transient absorption experiments will be discussed, and compared with the comparative chemicurrent yields for the two steady state reactions.

[1] S.N. Maximoff and M. Head-Gordon, Proc. Natl. Acad. Sci. USA (in press, 2009).

[O-2]

Do We Really Need DFT?
Alternative Correlated Orbital Theories From Wavefunction Theory

Rodney J. Bartlett, Monika Musial, Ajith Perera, Prakash Verma
University of Florida

Because of the ability to incorporate electron correlation into the description of molecules, in a procedure that is computationally equivalent to a Hartree-Fock mean field calculation; Kohn-Sham DFT methods have become the choice for most large scale applications. However, they lack the rigor of correlated wavefunction theory, as manifested in coupled-cluster theory. Unlike DFT, the latter is guaranteed to converge to the right answer in the limit of basis set and electron correlation---and for the right reason. This raises the question of whether alternative, correlated orbital approaches based solely within wavefunction theory can offer similar computational advantages.
In this talk we will offer a correlated orbital theory (COT) that is based upon the condition that all principal ionization potentials and electron attached energies, including the unbound ones, are exact. Unlike DFT which suffers from problems with self-interaction, local potentials, charge-transfer, and dispersion interactions; the correlated one-particle theory we propose has none of these limitations, and, in fact, it can always be implemented with coupled-cluster theory. Its existence is thus established by construction, not by existence theorems. However, to make it computationally comparable to DFT, its development will require good approximations for two-electron effects, but without the limitation to their being a functional of the density or local. Furthermore, it will offer a litmus test to any such approximation, as the equations incorporating the approximation must provide the exact principal ionization potentials and electron attachments. The theory will be presented and some initial applications.

[O-3]

Restricted active space second order perturbation theory (RASPT2) versus CASPT2 for the treatment of non-dynamical electron correlation

Laura Gagliardi
Department of Physical Chemistry
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30, Quai Ernest Ansermet
CH-1211 Geneva Switzerland
and
Department of Chemistry
University of Minnesota
207 Pleasant St. SE
Minneapolis MN

Chemical systems with a multiconfigurational electronic structure continue to represent a major challenge for modern quantum chemistry. The CASSCF/CASPT2 approach [1] is one of the most elegant ways to treat non-dynamical electron correlation; however, it is severely limited by the size of the active space, which may include at most 15-16 electrons in 15-16 active orbitals.

We have recently extended this method to the restricted active space RASSCF/RASPT2 regime [2], which permits the address of significantly larger active spaces, including up to 30 electrons in 30 orbitals, by considering more limited sets of excitations.

In this lecture I will describe the RASPT2 method and I will show our recent applications concerning the study of supported CunO2 systems (n = 1, 2) [3] and organic oligomers of increasing size [4].

[1] B. O. Roos, P. R. Taylor, and P. E. M. Siegbahn, Chem. Phys. 48, 157 (1980); B. O. Roos, in Advances in Chemical Physics: Ab Initio Methods in Quantum Chemistry-II, Wiley, Chichester, England, (1987), Chap. 69, p. 399.
[2] P.-A. Malmqvist, K. Pierloot., A. R. Moughal Shahi, C. J. Cramer and L. Gagliardi The Restricted Active Space followed by second order perturbation theory method: theory and application to the study of CuO2 and Cu2O2 systems J. Chem. Phys. 128, 204109 (2008)
[3] S. M. Huber, A. R. Moughal Shahi, F. Aquilante, C. J. Cramer, and L. Gagliardi What Active Space Adequately Describes Oxygen Activation by a Late Transition Metal? CASPT2 and RASPT2 Applied to Intermediates from the Reaction of O2 with a Cu(I)-α-Ketocarboxylate submitted (2009)
[4] A. R. Moughal Shahi, F. Aquilante, C. J. Cramer, and L. Gagliardi Organic oligomers of increasing size represent a challenge for the CASPT2 method, while they can be addressed with the RASPT2 approach in preparation (2009)

[O-4]

Fragmentation Methods: Accurate Calculations For Large Molecular Systems

Mark S. Gordon
Iowa State University

Two recent fragmentaion methods, the symmetric fragmentation method (SFM)and the fragment moelcular orbital (FMO) method both facilitate the accurate calculation of accurate molecular energies for large molecular systems. Following a summary of the theory for each method, illustrative examples will be presented.

[O-5]

Efficient Atomic Simulation of Solvent Effects

Peter Pulay,[1] *Tomasz Janowski*[1], *Michel Dupuis*[2]

[1]Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR 72701, USA

[2]Chemical Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99352

A highly efficient method is introduced for QM/MM calculations with electronic embedding. It obviates the need to perform a high-level electronic structure calculation for every solvent or environment configuration. The response of the system to the long-range electrostatic field of the environment is evaluated using precalculated generalized electric moments and polarizabilities. The latter are the first and second order responses of the system to spatially modulated electric fields. In our current implementation, the electric potential of the surrounding is evaluated on a grid within the molecule and fitted to a set of trigonometric functions defined in a box larger than the molecule. Calculation of the total response from precalculated responses is several orders of magnitude faster than a new electronic structure calculation[1].

The main projected use of this method is to perform thermodynamic simulations, mainly Monte Carlo simulations in solutions. Solvent effects are very important, particularly for reactions that involve charge separation (see, for instance[2]). Reliable statistics, which requires averaging over millions of configurations, can be collected efficiently using data from a limited number of high-level calculations. A similar method, restricted to first-order, has been previously suggested by Shiga and Tachikawa[3]. These authors recalculate the relevant electron-nucleus electrostatic interaction matrix elements. This gives exact first-order results but becomes expensive for large basis sets, and cannot handle polarizability terms.

[1]T. Janowski, P. Pulay, Efficient Calculation of the Energy of a Molecule in an Arbitrary Electric Field, Int. J. Quantum Chem., 2009, http://www3.interscience.wiley.com/journal/29830/home (Hirao Volume)

[2]M. Ohisa, H. Yamamoto, M. Dupuis, and M. Aida, Phys. Chem. Chem. Phys. 2008, 10, 844.

[3]M. Shiga, M. Tachikawa, Ab initio Quantum Mechanical Molecular Mechanical Molecular Dynamics using Multiple Time-Scale Approach and Perturbation Theory, Molecular Simulation 2007, 33, 171.

[O-6]

Linear Scaling Quantum Mechanics Methods for Molecules and Materials

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Advances in *ab initio* linear scaling quantum mechanics algorithms for molecules (multi-reference single and double excitation configuration interaction, MRSDCI) and materials (orbital-free density functional theory, OFDFT) will be discussed. MRSDCI typically scales as $O(N^6)$, but through a series of numerical approximations that do not degrade accuracy, we have reduced the scaling all the way to *linear*. Further acceleration of the algorithm has been achieved very recently via introduction of a Cholesky decomposition of the integrals and an orthogonal virtual orbital basis. We have systematically eliminated bottlenecks within OFDFT to render the entire algorithm linear scaling for all system sizes (no crossover point). When nonlocal kinetic energy density functionals are employed, OFDFT can be as accurate as Kohn-Sham DFT for predicting properties of main group metals. With parallelization introduced via domain decomposition, we can use quantum mechanics to study samples containing 10^4-10^6 atoms with a modest number of processors. As defects that control behavior in real metal samples contain at least thousands of atoms embedded in bulk samples containing orders of magnitude more atoms, computer simulations of such features has been limited to classical force field descriptions, which are not easily extended to multicomponent alloys. Now we can study such features with OFDFT, so that predictions can be made independent of experiment and optimal alloy design from first principles can be pursued. Thus, applications of these two methods range from describing accurately the breaking of chemical bonds in large molecules to mechanical properties of bulk metal alloys containing large scale defects such as dislocations, cracks, and grain boundaries. We validate these methods against more exact theories and/or experiment as well as gain new insights into the behavior of materials. We are beginning to use these two techniques to characterize combustion thermochemistry of large molecules such as those present in biofuels and to characterize mechanical properties of aluminum and magnesium alloys sought for lightweight, fuel efficient vehicle construction.

Selected References

[1] L. Hung and E. A. Carter, "Accurate Simulations of Metals at the Mesoscale: Explicit Treatment of 1 Million Atoms with Quantum Mechanics," Chem. Phys. Lett. Frontier Article, in press (2009).

[2] T. S. Chwee, A. B. Szilva, R. Lindh, and E. A. Carter, "Linear Scaling Multireference Singles and Doubles Configuration Interaction," J. Chem. Phys. **128**, 224106 (2008).

[O-7]

Orbital magnetization and magnetoelectric phenomena in solids

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The precise definition of the orbital magnetization in a periodic solid, including possible interstitial contributions, turns out to be a subtle issue. I will first present our recently developed theory of orbital magnetization, which uses a Wannier representation to derive a practical k-space implementation [1-2]. I will also summarize recent calculations of the orbital magnetization in Fe, Ni, and Co [3], and describe a converse approach to the computation of NMR shieldings using the orbital-magnetization methodology [4]. In the last part of the talk, I will discuss some aspects of the theory of topological quantum-Hall and quantum-spin-Hall insulators, in which orbital magnetoelectric effects play a central role [5].

References

[1] T. Thonhauser, D. Ceresoli, D. Vanderbilt, and R. Resta, Phys. Rev. Lett. **95**, 137205 (2005).
[2] D. Ceresoli, T. Thonhauser, D. Vanderbilt, and R. Resta, Phys. Rev. B **74**, 024408 (2006).
[3] D. Ceresoli, U. Gerstmann, A.P. Seitsonen, and F. Mauri, http://arxiv.org/abs/0904.1988.
[4] T. Thonhauser, D. Ceresoli, A.A. Mostofi, N. Marzari, R. Resta, and D. Vanderbilt, http://arxiv.org/abs/0709.4429.
[5] A. Essin, J.E. Moore, and D. Vanderbilt, Phys. Rev. Lett. **102**, 146805 (2009).

[O-8]

Coloring the noise

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Sampling the canonical distribution function is one of the main tasks in the simulation of equilibrium many body systems. One way of achieving this is to use Langevin dynamics, a fact that has long been recognized, and widely exploited. Langevin equations are characterized by the presence of a dissipative term proportional to the instantaneous velocities which is compensated by an uncorrelated random force (white noise). Much less known and hardly ever used is a generalization of Langevin equations in which the dissipative term contains a memory function and the noise is correlated (colored noise). Using this generalization we introduce a number of new powerful sampling methods. In particular we show that it is possible to considerably enhance sampling speed and quite remarkably we can induce a quantum behavior at negligible computational cost. A number of applications will be presented.

[O-9]

Solvation and transport of charged topological defects in water, vacuum/water interfaces, and other hydrogen-bonded media.

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The ability of hydrogen-bonded liquids such as water to support anomalous diffusion mechanisms of charged defects created by the addition or removal or protons plays a vital role in a variety of processes of chemical, biological, and technological importance. Transport of hydronium (H_3O^+) and hydroxide (OH^-) ions in aqueous solution is fundamental in the behavior of acids and bases and underlies proton pumping and enzyme catalytic processes. Proton transport in methanol and methanol/water mixtures is important in the operation of methanol based fuel cells using proton-exchange membranes. In this talk, an in-depth investigation of the underlying transport mechanisms in water, vacuum/water interfaces, and other hydrogen-bonded media using *ab initio* molecular dynamics and *ab initio* path integral techniques will be presented. These techniques employ electronic structure (density functional) calculations performed ``on the fly", from which internuclear forces are obtained. In order to ensure accuracy of the calculations, we have developed a new basis-set approach that allows the electronic structure calculations to be performed in a fully converged or complete basis set. In addition, some of the calculations also employ empirical dispersion corrections. The results indicate that anomalous proton transport requires the occurrence of certain solvent fluctuations that place the proton-receiving moieties in a solvation state that resembles the species they will become after the proton transfer is complete. Other important patters of behavior as well as crucial differences among different systems will be highlighted. Finally, several new analysis techniques will be presented, including a chemical master-equation approach for extracting relevant time scales and a graph-theoretic scheme for analyzing the connectivity of hydrogen-bonded networks.

[O-10]

Analytical coarse-grained theories to bridge timescales in the dynamics of macromolecular systems

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Macromolecular liquids are complex fluids characterized by an extended range of time scales where dynamical processes occur. Theoretical models and computer simulations are limited in the range of time scales they can describe. Coarse-graining and multiscale modeling procedures can alleviate this problem.
The unique perspective of our research is the focus on developing first-principles analytical approaches, as opposed to numerical solution, for the coarse-graining and modeling of complex macromolecular systems.[1]

We will present, first, an analytical coarse-grained approach and a multiscale procedure derived from the solution of the Ornstein-Zernike equation, to describe the structure of polymer liquids and their mixtures across the length scales of interest.[2]

Second, an analytical rescaling approach allows for the direct measurement of "real" dynamics from mesoscale simulations of a coarse-grained polymer liquid. The rescaling procedure is obtained from the approximated solution of the memory kernels, and friction coefficients, for both the atomistic and the coarse-grained representations.

Finally, Generalized Langevin Equations (GLE) for coarse-grained models of macromolecular structures can describe their dynamics across many orders of magnitude in time. Specifically, using projection operator techniques a GLE is obtained that describes the sub-diffusive regime in dynamically heterogeneous polymer liquids, in quantitative agreement with Neutron Spin Echo experiments.[3] A new model for the hydrodynamic interaction (Oseen tensor) is included in our GLE for the dynamics of a protein in solution, which predicts internal relaxation of proteins in good agreement with NMR T1, T2, and NOE measurements as well as with X-ray Debye-Waller factors.[4]

1) M. G. Guenza "Theoretical Models to Bridge Time Scales in Polymer Dynamics" Journal of Physics: Condensed Matter 20, 033101-0331024 (2008).

2) E. J. Sambriski, M. G. Guenza "Theoretical coarse-graining approach to bridge length scales in diblock copolymer liquids" Phys. Rev. E 76, 051801-051813 (2007).

3) M. Zamponi, A. Wischnewski, M. Monkenbusch, L. Willner, D. Richter, P. Falus, B. Farago, and M. G. Guenza "Cooperative dynamics in homopolymer melts: a comparison of theoretical predictions with Neutron Spin Echo experiments" J. Phys. Chem. B 112, 16220-162229 (2008).

4) Esther Caballero-Manrique, Jenelly K. Brey, William A. Deutschman, Fredrick W. Dahlquist M. G. Guenza "A Theory of Protein Dynamics to predict N.M.R. relaxation" Biophysical Journal 93, 4128-4140 (2007).

[O-11]

Moving in a Crowded World

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The interior of a biochemical cell is complex. It contains a variety organelles, filaments and other macromolecular obstacles that influence the dynamics and affect the biological function of proteins and other biomolecules. Such cells are said to be crowded since the concentration of obstacles is high and no one species dominates. Dynamical processes in such media are very different from those in simple bulk systems because of the severe restriction on the available volume and the importance of surface effects. Modeling the dynamics of such complex systems is most effectively carried out using mesoscopic methods since the physically relevant distance and time scales are often very long. Using one such method, multiparticle collision dynamics, as a simulation tool, the talk will describe how reaction and transport change as a result of molecular crowding and how polymer molecule conformational and translational motions are influenced by confining geometries due to the presence of obstacles.

[O-12]

Combining quantum dynamics and quantum chemistry for reactions of polyatomic molecules

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This lecture will describe new research in our group on linking quantum dynamics and quantum chemistry methods to predict the kinetics and dynamics of reactions of polyatomic molecules from first principles. A reduced dimensionality approach is used that combines accurate quantum chemistry calculations of a small number of key points on the potential energy surface with a quantum-dynamical treatment of the bonds being broken and formed in a chemical reaction. Applications to abstraction reactions of H atoms with molecules such as CH4, C3H6 and CH3NH2 will be described together with calculations on the CH3 + CH4, and Cl +CH4 reactions. Recent improvements of the theory for treating spectator modes developed by Dr Simon Banks in our group will also be described as will the extension of the approach to reactions on solid surfaces.

The calculations have been done in our group by Boutheina Kerkeni, Christopher Tautermann, Simon Banks and Sarah Remmert.

[O-13]

Nuclear-Electronic Orbital Approach: Electron-Proton Correlation and Multicomponent Density Functional Theory

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Recent advances in the development of the nuclear-electronic orbital (NEO) approach will be presented. In the NEO approach, selected nuclei are treated quantum mechanically on the same level as the electrons with molecular orbital techniques. For hydrogen transfer and hydrogen bonding systems, typically the hydrogen nuclei and all electrons are treated quantum mechanically. Electron-proton dynamical correlation is highly significant because of the attractive electrostatic interaction between the electron and the proton. An explicitly correlated Hartree-Fock scheme has been formulated to include explicit electron-proton correlation directly into the nuclear-electronic orbital self-consistent-field framework with Gaussian-type geminal functions. A multicomponent density functional theory has also been formulated, and electron-proton functionals have been developed based on the explicitly correlated electron-proton pair density. Initial applications illustrate that these new methods provide accurate nuclear densities, thereby enabling calculations of a wide range of molecular properties. Recently the NEO method has been combined with vibronic coupling theory to calculate hydrogen tunneling splittings in polyatomic molecules. In this NEO-vibronic coupling approach, the transferring proton and all electrons are treated quantum mechanically at the NEO level, and the other nuclei are treated quantum mechanically using vibronic coupling theory. This approach is computationally practical and efficient for relatively large molecules. The calculated tunneling splitting for malonaldehyde is in excellent agreement with the experimental value. Furthermore, this approach enables the identification of the dominant modes coupled to the transferring hydrogen motion and provides insight into their roles in the hydrogen tunneling process.

[O-14]

New strategies for solving the vibrational Schrödinger equation

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In the last ten years the use of (multidimensional) contracted basis functions and the Lanczos algorithm have made it possible to compute vibrational (and rovibrational) spectra of molecules with as many as 6 atoms. Further progress is hampered by the use of huge direct product Gauss quadrature grids. In this talk, I shall briefly outline three new approaches for obviating the direct product grid. The first approach is applicable if the potential is a sum of products. It exploits this structure to facilitate evaluating the matrix-vector products required to use the Lanczos algorithm to compute a spectrum. The second approach uses collocation (no integrals are computed), neural network "basis functions", and a rectangular eigensolver. In the third approach, ideas of Smolyak are used in conjunction with new quadrature schemes to reduce, by orders of magnitude, the number of required points. Applications of these ideas to model problems, H2O and SF6 will be presented.

[O-15]

QM/QM Electronic Embedding Models for Materials Chemistry

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The development of accurate and broadly applicable models for large molecules/materials continues to be a significant challenge in quantum chemistry. Hybrid models, such as the popular ONIOM-based QM/QM schemes (where the central region and the surrounding region are partitioned and treated with two different levels of theory), offer a promising avenue for modeling large systems. However, most QM/QM applications typically use only a mechanical embedding scheme where the wavefunction in the central region is unaffected by the electronic structure of the surrounding region. We are presently developing a sequence of electronic embedding schemes for more realistic simulations. The resulting hierarchy, where the treatment ranges from simple point charge embedding to interaction integrals in the Hamiltonian matrix, will be discussed. We will also describe our current development status and present results from initial applications to materials studies.

[O-16]

Exploring Potential Energy Surfaces Using Ab Initio Molecular Dynamics

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In Born-Oppenheimer molecular dynamics (BOMD), each time the forces on the nuclei are needed in the integration of the classical equations of motion, a converged electronic structure calculation is carried out. In extended Lagrangian molecular dynamics, such as Car-Parrinello MD (CPMD) or atom-centered density matrix propagation MD (ADMP), the electronic structure is propagated classically rather than converged. AIMD studies of acetone radical cation, pentanedione radical cation,allene dication and methyleneimine neutral, monocation and dication will be discussed. For molecules in intense laser fields, the electron density must be propagated quantum mechanically. Molecular systems can be treated with time-dependent Hartree-Fock or density functional theory (TD-HF or TD-DFT) and with time-dependent configuration interaction (TD-CIS and TD-EOMCC). The response of a butadiene in short intense laser pulses will be described.

[O-17]

The Role of Radicals in Coenzyme-B_{12}-Mediated Reactions: A Computational Approach

Leo Radom, David M. Smith, Gregory M. Sandala, Boris Kovacevic, Danijela Baric, Bo Durbeej, Denis Bucher, Stacey D. Wetmore, Michelle L. Coote, Bernard T. Golding, and Neil Marsh
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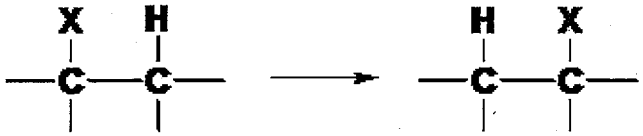
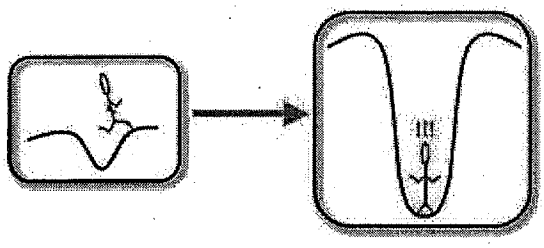
In the presence of the appropriate enzyme, coenzyme B_{12} mediates reactions that have a remarkably simple form, namely the formal interchange of a group X and a hydrogen on adjacent atoms:



We have used high-level computational quantum chemistry calculations to study a selection of such reactions and this has provided valuable insights into the mechanism. We find that radicals play a crucial role in these reactions, both in their activation and in their deactivation.[1] Highlights from our recent research will be presented.



1. For recent studies, see for example: (a) Sandala, G. M.; Smith, D. M.; Coote, M. L.; Radom, L. *J. Am. Chem. Soc.*, **2004**, *126*, 12206–12207. (b) Sandala, G. M.; Smith, D. M.; Radom, L. *J. Am. Chem. Soc.*, **2005**, *127*, 8856–8864. (c) Sandala, G. M.; Smith, D. M.; Coote, M. L.; Golding, B. T.; Radom, L. *J. Am. Chem. Soc.*, **2006**, *128*, 3433–3444. (d) Sandala, G. M.; Smith, D. M.; Radom, L. *J. Am. Chem. Soc.*, **2006**, *128*, 16004–16005. (e) Sandala, G. M.; Smith, D. M.; Marsh, E. N. G.; Radom, L. *J. Am. Chem. Soc.*, **2007**, *129*, 1623–1633. (f) Sandala, G. M.; Smith, D. M.; Radom, L. *J. Am. Chem. Soc.*, **2008**, *130*, 10684–10690. (g) Sandala, G. M.; Kovacevic, B.; Baric, D.; Smith, D. M.; Radom, *Chem. Eur. J.*, **2009**, *in press*.

[O-18]

Accurate Interaction Energies of Building Blocks of Biomacromolecules and the Role of Dispersion Energy

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Structures and stabilization energies of molecular clusters playing a role in biodisciplines are investigated. Specifically, we consider H-bonded and stacked structures of DNA base pairs and amino acid pairs in a gas phase and in an environment. Benchmark stabilization energies of complexes studied are determined as the Complete Basis Set (CBS) limit of the CCSD(T) calculations and various constructions of these energies are discussed.The role of CCSDT and CCSD(TQ) is also considered. Stabilization energies of stacked structures originates in London dispersion energy and only high-level wave function and density functional theories (WFT, DFT) can be applied.The performance of various recently introduced modification of the WFT and DFT methods is briefly discussed. The unique role of dispersion energy in stabilizing the structure of biomacromolecules is stressed.

[O-19]

A Neo-Classical EPIC on Electronic Polarization for Biomolecular Simulations

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(b) OpenEye Inc.
(c) Universite de Montreal
(d) University of Chicago

A novel classical approach for intramolecular polarizability is introduced: the Electronic Polarization from an Internal Continuum (EPIC) model. We show that Poisson's equation alone can completely and accurately account for both isotropic and anistropic molecular polarizabilities for a large, diverse and challenging range of organic species. In contrast to other classical approaches to electronic polarization, this simple and general model avoids the polarizability catastrophe while using very few fitted parameters and without resorting to auxiliary sites or anisotropic atomic centers. The peculiarly high internal dielectric constant required is validated by the comparison of macroscopic dielectric constants calculated from liquid simulations to experimental values based on refractive indices. With the goal of incorporating this method into a polarizable force field, least-squares fitting of atomic charges to quantum mechanical electrostatuc potentials has been recast to accommodate the internal dielectric (DRESP). With EPIC polarizatoin and DRESP charges, challenging cases for polarized intermolecular interactions are shown to be well reproduced. The method also lends itself to continuum solvation calculations, as demonstrated by good performance in calculating experimental hydration free energies. We envision this model for electrostatics forming the foundation for a simple, general, and accurate polarizable force field suitable for biomolecular simulations.

[O-20]

Alzheimer's Disease - Chemical Causes and Prevention

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Alzheimer's disease is a complex, fatal, neurological disorder brought on largely by old age, and characterized by the presence of extracellular senile plaques and intracellular fibrillary tangles. The brain is besieged by oxidative stress, metal sequestration, membrane damage, and blocked neuronal receptors. The damaging agent is an oligomeric form of a 40-42 residue peptide, A&beta. For the last decade, we have investigated computationally the chemical causes of the neurotoxicity of A&beta. Our initial working hypothesis, *Radical Theory of Alzheimer's Disease*, rationalized all of the chemistry of Alzheimer's disease as it was understood a decade ago. While the model has evolved over time, the radical chemistry required for the hypothesis has been readily amenable to computational investigations, from the initiating copper-peptide complexes, to methionine oxidation and glycyl backbone radical generation, to the first steps of lipid peroxidation by which neuronal and mitochondrial cell membranes are destroyed. We have also examined by molecular dynamics simulations the structures of Aβ and polyunsaturated membranes, and the energetics of peptide-peptide interactions that mediate the self-aggregation of Aβ into neurotoxic oligomers. This talk will highlight some of this work and point to promising directions for the development of drugs that may prevent Alzheimer's disease, or at least delay its onset.

[O-21]

X-Pol Potential: From Lifson Molecular Mechanics to Quantal Force Field for Biomolecular Simulations

Jiali Gao
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At the heart of dynamics simulations is the potential energy function that describes intermolecular interactions in the system, and often it is the accuracy of the potential energy surface that determines the reliability of simulation results. The current generation of force fields was essentially established in the 1960s. While the accuracy has been improved tremendously by systematic parameterization, little has changed in the formalism and in the representation of the system. The explicit polarization (X-Pol) potential is a quantal force field based on electronic structure theory, designed for molecular dynamics simulation and modeling of biopolymers. In this approach, molecular polarization and charge transfer effects are explicitly treated by an electronic structure method, and the wave function of the entire system is variationally optimized. We illustrate the possibility of parametrizing the X-Pol potential to achieve the desired accuracy as that in MM force fields, and demonstrate the feasibility of carrying out molecular dynamics (MD) simulation of solvated proteins. We use a system consisting of 14281 atoms and about 30,000 basis functions, including the protein bovine pancreatic trypsin inhibitor (BPTI) in water with periodic boundary conditions, to show the efficiency of an electronic structure-based force field in atomistic simulations. The performance of the X-Pol potential is also examined using ab initio molecular orbital theory and density functional theory. The X-POL force field permits the inclusion of time-dependent quantum mechanical polarization and charge transfer effects in much larger systems than was previously possible.

[O-22]

Progress and Challenges in Modeling Organic and Biomolecular Systems

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There has been great progress in the realistic modeling of organic and biomolecular systems over the last thirty years. Our contributions have focused on enhancing the evaluation of the energetics of molecular systems, simulations of reactions in condensed phases to elucidate mechanisms and solvent effects on reaction rates, computation of free-energy changes for equilibria including host-guest binding, and *de novo* molecular design. Examples of the state-of-the-art in each area will be presented including our use of free-energy calculations to guide lead optimization in inhibitor design. Current challenges will also be discussed.

Recent References:
Efficient Drug Lead Discovery and Optimization. Jorgensen, W. L. *Acc. Chem. Res.* 2009, *42*, 724-733.

Perspective on Free-Energy Perturbation Calculations for Chemical Equilibria. Jorgensen, W. L.; Thomas, L. L. *J. Chem. Theory Comput.* 2008, *4*, 869-876.

Performance of the B3LYP Density Functional Method for a Large Set of Organic Molecules. Tirado-Rives, J.; Jorgensen, W. L. *J. Chem. Theory Comput.* 2008, *4*, 297-306.

[O-23]

Towards the multiscale modeling of biological systems and processes – progress on RNA polymerase and transcription

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One viewpoint (as expressed by Sui Huang) of the still emerging field of systems biology sees integration along an axis involving system size (and perhaps some dynamics) going from macromolecules (proteins, DNA, RNA, etc) to cells, to tissues, to organs, to organisms, etc. This is sometimes called computational biology. Another axis looks at kinetic models at growing levels of complexity going from pathways, to modules to full genetic regulatory networks. This is taken to lie in the general field of bioinformatics. There is an almost unpopulated chasm between the two communities pursuing these two approaches.

In this lecture I will argue that a starting point at even a finer level of resolution is necessary if one is to fill the gap between the two axes. I will attempt to describe the state-of-the-art of atomistic multi-scale approaches including those that use quantum mechanics to describe chemical reactions. I will give a few results for nano-bio systems that are now being calculated using Density Functional Theory (DFT). Although modern DFT is fast, it is still not fast enough for applications in biology so we are paying attention to so-called reactive force fields (ReaxFF) which try to capture the essence of quantum mechanical calculations through parameterization against DFT calculations on full chemical reaction paths.

Turning to the other axis, I will summarize recent results on protein production regulated by genetic networks that incorporate the main steps in the transcription and translation processes. The stochastic Gillespie (Kinetic Monte Carlo - KMC) algorithm is used to solve the (effective) chemical master equation.

The seminar will finish with our first (baby-step) attempts to fill the gap by looking at the mechanism of transcription involving metallo-proteins with Mg ions in the active site. The project uses DFT, ReaxFF along with phenomenological KMC simulations. We hope, in the fullness of time, to be able to feed calculated information on reaction rates into the Gillespie (or other) algorithm and, hence, have the behavior of the regulatory network guided by the underlying atomistic and electronic mechanisms, and vice-versa in a bottom-up – top-down approach to the problem.

[O-24]

Insights and Progress in Density Functional Theory.

Weitao Yang
Duke University Professor of Chemistry

Density functional theory of electronic structure is widely and successfully applied in simulations throughout engineering and sciences. However, there are spectacular failures for many predicted properties. The errors include underestimation of the barriers of chemical reactions, the band gaps of materials, the energies of dissociating molecular ions and charge transfer excitation energies. Typical DFT calculations also fail to describe degenerate or near degenerate systems, as arise in the breaking of chemical bonds, and strongly correlated materials. These errors can all be characterized and understood through the perspective of fractional charges and fractional spins introduced recently. Standard approximations for the exchange-correlation functional have been found to give big errors for the linearity condition of fractional charges, leading to delocalization error, and the constancy condition of fractional spins, leading to static correlation error. These two conditions have been unified and extended to states with both fractional charge and fractional spin to give a much more stringent condition: the exact energy functional is a plane, linear along the fractional charge coordinate and constant along the fractional spin coordinate with a line of discontinuity at the integer. Violation of this condition underlies the failure of known approximate functionals to describe the gaps in strongly correlated systems. It is shown that explicitly discontinuous functionals of the density or orbitals that go beyond these currently used smooth approximations is the key for the application of density functional theory to strongly correlated systems. Understanding the errors of functionals in the simplest way possible --- as violations of exact conditions for fractional charges and fractional spins -- opens the path forward for reduction of the errors and for applications of density functional theory in new frontiers.

References

P. Mori-Sanchez, A. J. Cohen, and W. T. Yang, "Self-interaction-free exchange -correlation functional for thermochemistry and kinetics," J. Chem. Phys. 124:91102, 2006.

A. J. Cohen, P. Mori-Sanchez, and W. T. Yang, "Insights into current limitations of density functional theory," Science, 321:792, Aug 2008.

A. J. Cohen, P. Mori-Sanchez, and W. T. Yang, "Fractional charge perspective on the band gap in density-functional theory," Physical Review B, 77:115123, 2008.

P. Mori-Sanchez, A. J. Cohen, and W. T. Yang, "Localization and delocalization errors in density functional theory and implications for band-gap prediction," Phys. Rev. Lett. 100:146401, 2008.

A. J. Cohen, P. Mori-Sanchez, and W. T. Yang, "Fractional spins and static correlation error in density functional theory," Journal of Chemical Physics, 129:121104, 2008.

E. R. Johnson, P. Mori-Sanchez, A. J. Cohen, and W. T. Yang, "Delocalization errors in density functionals and implications for main-group thermochemistry," Journal of Chemical Physics, 129:204112, 2008.

P. Mori-Sanchez, A. J. Cohen, and W. T. Yang, "Discontinuous nature of the exchange-correlation functional in strongly correlated systems," Phys. Rev. Lett. 102:066403, 2009.

A. J. Cohen, P. Mori-Sanchez, and W. T. Yang, "Second-order perturbation theory with fractional charges and fractional spins," J. Chem. Theory Comput., 5:786, 2009.

A. J. Cohen, P. Mori-Sanchez, and W. T. Yang, "Failure of the random phase approximation correlation energy," J. Chem. Phys., 2009. submitted (arXiv:0903.4403v1)

[O-25]

Workhorse Semilocal Density Functional for Condensed Matter Physics and Quantum Chemistry

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The TPSS meta-generalized gradient approximation [1] was designed to be computationally efficient (semilocal) and applicable to a broad array of electronic systems. It gave accurate total energies, atomization energies of molecules, and surface energies for solids. However, it only slightly improved the too-long lattice constants of solids predicted by the standard PBE GGA [2]. (Because solids are softer than molecules, the prediction of their geometries makes greater demands on a density functional.) Recently we proposed a PBEsol GGA [3] that restored the gradient expansion for exchange over a wide range of densities, and so improved lattice constants of solids while worsening atomization energies. Here we construct a revised TPSS [4] (revTPSS) meta-GGA that combines all the TPSS exact constraints with the new insight from PBEsol, and so gives good lattice constants, atomization energies, and surface energies.

[1] J. Tao, J.P. Perdew, V.N. Staroverov, and G.E. Scuseria, Phys. Rev. Lett. 91, 146401 (2003).
[2] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[3] J.P. Perdew, A. Ruzsinszky, G.I. Csonka, L.A. Constantin, X. Zhou, O.A. Vydrov, G.E. Scuseria, and K. Burke, Phys. Rev. Lett. 100, 136406 (2008).
[4] J.P. Perdew, A. Ruzsinszky, G.I. Csonka, L.A. Constantin, and J. Sun, submitted.

[O-26]

New models for mixing wavefunctions with density functional theory

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The recent realization that the ground-state correlation energy of the random phase approximation (RPA) is intimately connected to an approximate coupled cluster doubles (CCD) model [1], opens interesting avenues for mixing RPA with DFT [2].

I will also present a two-particle density matrix ansatz that seems particularly well-suited for describing static (and only static) correlation [3]. Dynamical correlation functionals for this model are non-trivial and I will discuss progress on this front.

Keywords: RPA, range-separation, static correlation

[1] G. E. Scuseria, T. M. Henderson, and D. C. Sorensen, J. Chem. Phys. 129, 231101 (2008).
[2] B. G. Janesko, T. M. Henderson, and G. E. Scuseria, J. Chem. Phys. 130, 081105 (2009).
[3] T. Tsuchimochi and G. E. Scuseria, submitted for publication.

[O-27]

Electrons passing through molecules

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For a variety of phenomena in chemistry, the current density of electrons is the key variable. Examples include metastable anions that emit electrons at a certain rate, giving rise to a current density of outgoing electrons. In STM imaging of molecules on surfaces, electrons pass through the system. This process is closely related to the coherent electron transport that occurs in molecular electronic devices. In both cases, the current density is the central quantity.

We explain various techniques to model the problems mentioned above. First, we consider Green's function methods and apply them [1], for instance, to analyze experiments on photo switches where molecules are transformed from a conducting to a non-conducting isomer by means of light. Second, we present a theory based on a non-Hermitian model Hamiltonian [2,3,4] for the description of open systems that exchange current density with their environment. This approach is ideally suited to unravel qualitative relationships between molecular structure and current density. An application of our model Hamiltonian deals with polyacenes. We find that electron transmission through these systems is hindered despite of the delocalized π orbitals. This behavior is shown to be a precursor of the peculiar properties of graphene.

To account for electron correlation effects, we extend [5] our model Hamiltonian theory by introducing a finite, many-electron basis of Slater determinants. Also ground-state density functional theory is adapted to the domain of open systems. These methods allow us to consider the impact of electron interaction, giving rise to phenomena such as coulomb drag.

[1] M. Zhuang, M. Ernzerhof, J. Chem. Phys. 130, 114704 (2009).
[2] F. Goyer, M. Ernzerhof, M. Zhuang, J. Chem. Phys. 126, 144104 (2007).
[3] M. Ernzerhof, J. Chem. Phys. 127, 204709 (2007).
[4] P. Rocheleau, M. Ernzerhof, J. Chem. Phys. 130, 184704 (2009).
[5] A. Goker, F. Goyer, M. Ernzerhof, J. Chem. Phys. 129, 194901 (2008).

[O-28]

TIP4P, TTM2.1-F and AMOEBA water clusters: Evolution of properties of the global minima with size

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New algorithms for determining the global minima of hydrogen-bonded clusters are described. A novel combination of minima-hopping with translational and topology-modifying steps is used to locate putative global minima for clusters containing as many as 37 water molecules. It is applied first using the TIP4P force field, followed by reoptimization of as many as the lowest 2000 TIP4P structures using the AMOEBA and TTM2.1-F force fields. The structures of the global minima are examined with respect to the transition from regular to cage-like and clathrate-type structures as the cluster size increases. The evolution of other properties such as energy per monomer, ring distributions, and coordination numbers with cluster size is also traced. A comparison of the TIP4P, TTM2.1-F and AMOEBA force fields is presented.

[O-29]

Reinterpreting the Determinantal Ansatz in Kohn-Sham Theory. New Variational Approaches to Excited and (Nearly) Degenerate States in Density Functional Theory.

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Density functional theory in its Kohn Sham formulation is based on a single Slater determinant, an aspect shared with the single reference Couple-Cluster theories (1,2). The single determinantal KS-ansatz would appear to exclude the application of density functional theory to systems that even to zero order require a multi-reference representation in wave function mechanics.These are systems that exhibit a high degree of static correlation due to near or actual degeneracies. We shall discuss attempts made in our group (3,9) and elsewhere (10,13) to describe these systems within the KS-ansatz of a single determinant. It will also be shown how the reinterpretation of the determinantal ansatz can lead to an approoach that determines excitation energies variationally (14,16). To lower (second) order, excitation energies obtained from the variational approach are equivalent to those from time-dependent density functional theory (16).However,to higher order, the new approach affords a qualitatively correct picture of charge transfer transitions (14,15), even with regular GGA functionals.

References:

(1) A.I.Krylov. Chem.Phys.Lett. 2001,338,375. (2) A.I.Krylov. Chem.Phys.Lett. 2001,350,522. (3)T.Ziegler; A.Rauk and E.J. Baerends Theor.Chim.Acta 1977,43,261. (4) T.Ziegler in "Local Density Approximations in Quantum Chemistry and Solid State Physics" Edited by J.P.Dahl and J.Avery,,Plenum Press, New York 1984. (5) F.Wang and T.Ziegler J.Chem.Phys. 2004,121,12191. (6) F.Wang and T.Ziegler J.Chem.Phys. 2005,121,12191. (7)M. Seth and T. Ziegler, J. Chem. Phys. 2005,123, 144105. (8)M. Seth and T. Ziegler, J. Chem. Phys. 2006,124, 144105. (9)V.Tschinke and T.Ziegler J. Chem. Phys., 1990, 93, 8051 (10)A.Kazaryan, J.Heuver,M.Filatov J.Phys.Chem. 2009,ASAP (11)A. J. Cohen, P. Mori-Sánchez, W. Yang, Science 2008,321,792(12)M. A. Buijse, E. J. Baerends, J.Chem.Phys. 1990, 93, 4129-4141. (13)E. R. Johnson and A. D. Becke, J. Chem. Phys., 2008, 128, 124105.(14). Ziegler,T.; Seth,M.; Krykonov,M.; Autschbach,J. J. Chem. Phys. 2008, 129, 184114.(15)Ziegler,T.; Seth,M.; Krykonov,M.; Autschbach,J. J. Wang,F. Chem. Phys. 2009,submitted. (16) Ziegler,T.; Seth,M.; Krykonov,M.; Autschbach,J. J. Wang,F. Theochem. 2009,submitted.

[O-30]

Approaching the Hartree-Fock limit by perturbative methods

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I will describe three perturbative methods for improving finite-basis Hartree-Fock calculations toward the complete-basis limit. The best methods appear to offer quadratic error reduction and preliminary numerical applications using Jensen, Pople and Dunning basis sets demonstrate that remarkably accurate Hartree-Fock energies can be obtained. The relationship between these methods and the dual-basis schemes of Head-Gordon and co-workers will also be discussed.

[O-31]

Two-electron Reduced-Density-Matrix Mechanics:
With Application to Many-electron Atoms and Molecules

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In 1959 Charles Coulson popularized the challenge of computing the ground-state energy as a functional of the two-electron reduced density matrix (2-RDM) without the many-electron wavefunction. Recently, theoretical and computational advances have led to two classes of 2-RDM methods [1]: (i) the variational calculation of the 2-RDM subject to approximate N-representability conditions and (ii) the non-variational calculation of the 2-RDM from the anti-Hermitian contracted Schrödinger equation. I will develop the background for the 2-RDM methods, discuss recent theoretical and computational advances, and present some applications, including the detection of poly-radical correlation in polyaromatic acene chains, the treatment of protonated acetylene and malonaldehyde beyond the Born-Oppenheimer approximation, and the computation of energy barriers in the electrocylic conversion of bicyclobutane to *gauche*-1,3-butadiene.

[1] *Two-electron Reduced-Density-Matrix Mechanics with Application to Many-electron Atoms and Molecules*, edited by D. A. Mazziotti, Advances in Chemical Physics Vol. 134 (Wiley, New York, 2007).

[O-32]

Variational Reduced Density Matrix Theory: Successes and Failures

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Because the molecular Hamiltonian contains only one-body and two-body operators, the two-electron reduced density matrix contains all the information needed to evaluate the energy, as well as most of the other properties of interest to chemists and molecular physicists. A straightforward minimization of the energy is confounded by the N-representability problem, which can only be addressed approximately. The resulting theory has both advantages and disadvantages compared to more-traditional wavefunction-based approaches. The biggest advantage is that it performs well even when the molecule of interest has strong multireference character and the "Hartree-Fock plus correction" wavefunction paradigms fail. Also, as a lower-bound method, it provides a complementary tool to variational wavefunction approaches. The biggest disadvantages are the computational cost (which may yet be surmounted) and problems with dissociation and degeneracy that seem to afflict all approaches based on a "reduced" description of the system.

[O-33]

Modelling soft, hard and porous materials

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Computational materials science and *in silico* drug design, as well as, the widely diverse areas of biomodelling have all seen a very rapid boost during the last decade thanks to many new innovative tools and models now allowing phenomena from self-assembling to complex phase behavior to be routinely simulated. This talk will highlight our recent work in developing models and methods and applying them on complex systems. Specific studies discussed here include solubility of organic crystals, modelling of inner mitochondrial membranes, adsorption and separation of gas molecules in functionalized mesoporous silica and in zeolites, transport properties in liquid crystalline systems and nucleation of a mixture of L- and D-prolines in supersaturated DMSO solution.

[O-34]

A Projector Augmented Wave Formulation of the Optimized Effective Potential Formalism[a]

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The optimized effective potential (OEP) formalism has recently received renewed attention[1] as a method which can improve the accuracy of density functional calculations by representing orbital-dependent exchange-correlation functionals. Among other attributes, these can avoid self-interaction errors found in many explicit density-dependent exchange-correlation functionals. Since the Projector Augmented Wave (PAW) formalism[2] ensures accurate evaluation of Coulomb and exchange integrals by controlling their multipole moments,[3] it is a natural choice for implementing OEP within an efficient pseudopotential-like scheme. Focusing initially on the exact exchange functional, we have developed a frozen core approximation scheme for an atomic all-electron OEP formalism. The OEP exchange potential $V_x(r)$ can be partitioned into a well-localized core contribution $V_x^{core}(r)$ and a valence contribution $V_x^{vale}(r)$. In the PAW formulation, a valence exchange pseudopotential can be derived which converges to the frozencore valence potential $V_x^{vale}(r)$ outside the atomic spheres, while exchange effects within the atomic sphere are represented by atom-centered matrix elements. For the exact exchange functional, we have investigated the behavior of PAW-OEP basis, projector, and pseudopotential functions for several elements throughout the periodic table.

[1] S. Kümmel and L. Kronik, RMP **80**, 3 (2008).

[2] P. Blöchl, PRB **50** , 17953 (1994); N. A. W. Holzwarth *et al*, PRB **55** , 2005 (1997).

[3] J. Paier *et al*, JCP **122** , 234102 (2005).

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[O-35]

Imaginary and real time quantum dynamics with applications to weakly bound clusters

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Novel approaches for the study of molecular dynamics in complex systems will be presented. A particularly challenging problem is the inclusion of quantum mechanical effects in molecular simulations. We will first describe results for doped quantum clusters where one can observe the onset of superfluid behaviour at the nanoscale. Quantum Monte Carlo techniques are used in this case in order to obtain imaginary time correlation functions that can, in turn, be related to spectroscopic signatures. Approximate methods that allow the study of the more challenging problem of real time quantum dynamics will also be presented. Water clusters and other weakly bound systems will be used to illustrate these so-called semiclassical approaches.

[O-36]

Simulation of Ionic Liquids: How Ionic Structure Influences Macroscopic Behaviour

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Ionic liquids range from molten inorganic salts to room temperature ionic liquids, which are often composed of large organic cations combined with organic or inorganic anions. Room temperature ionic liquids are of importance for two reasons. Firstly, they have very different properties than common organic solvents and therefore are used as alternate solvents in chemical reactions. Secondly, they have the advantage of flexibility, because the solvent properties can be adjusted by altering the nature of the ionic constituents. However, it remains difficult to predict ionic liquid properties from the molecular structure of the ions. Our objective is to find and separate the ionic features that govern the liquid properties. In contrast to many simulation studies of ionic liquids, which employ all atom models, we focus on simpler model systems in order to isolate the influences of different molecular traits. Room temperature ionic liquids are often composed of ions that are very different in size, moreover, the charge of at least one of the ions is often ``located'' away from the center of mass. The influences of varying the ion size disparity and charge location on the liquid structure, the diffusion constants, the shear viscosity, and the electrical conductivity are determined by molecular dynamics simulations. It is shown that charge location is of particular importance, having significant effects on both structural and dynamical properties of ionic liquids. Some comparisons experiment will be discussed.

[O-37]

Multiscale Theories in Computational Chemistry: From Super CI and DFT for Electronic Structure to 3D Molecular Theory of Solvation and to Hydrodynamic Boundary Conditions

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A central part of genuine multiscale modeling is methodologies linking the scales through either force field parameters or effective interactions obtained theoretically/analytically and reflecting the physics and chemistry of the mutual effect of the scales. This talk will present recently developed methodologies that couple the scales of electronic structure of macromolecules, solvation structure of macromolecules and nanoarchitectures, and mass transport at nanoscale in nanofluidic systems with chemical specificities: (i) Super-CI approach to the multiconfigurational self-consistent field (MCSCF) approximation (implemented in the MOLCAS package), which provides superlinear scaling for large macromolecules [1]; (ii) SCF coupling of three-dimensional molecular theory of solvation [2] with *ab initio* (CASSCF/3D-RISM-KH) [3], and with density functional theory (KS-DFT/3D-RISM-KH) [4-6] and embedded DFT [7,8] (both implemented in the ADF package); (iii) Development of additive spherical site potential for exchange repulsion energy, based on intermolecular perturbation theory [9]; (iv) Coupling of 3D molecular theory of solvation with molecular dynamics simulation using multistep and Krylov subspace accelerators (MD/3D-RISM-KH, implemented in the Amber package) [10]; and (v) First-ever derivation and calculation of hydrodynamic boundary conditions (hydrodynamic slip length) for computational fluid dynamics from the first principles of statistical mechanics using a combination of linear response theory and equilibrium molecular theory of solvation [11-12].

References

[1] S. Gusarov, T. A. Fedorova, Yu. Yu. Dmitriev, and A. Kovalenko, Internat. J. Quantum Chem., **109**, 1672 (2009).
[2] A. Kovalenko, Three-dimensional RISM theory for molecular liquids and solid-liquid interfaces, in: *Molecular Theory of Solvation*, F. Hirata (Ed.) Series: Understanding Chemical Reactivity, P. G. Mezey (Ed.), vol.24, (Kluwer Academic Publishers, Dordrecht, 2003, 360 p.) pp.169-275.
[3] H. Sato, A. Kovalenko and F. Hirata, J. Chem. Phys., **112**, 9463 (2000).
[4] A. Kovalenko and F. Hirata, J. Chem. Phys., **110**, 10095 (1999).
[5] S. Gusarov, T. Ziegler, and A. Kovalenko, J. Phys. Chem. A, **110**, 6083 (2006).
[6] D. Casanova, S. Gusarov, A. Kovalenko, and T. Ziegler, J. Chem. Theory Comput., **3**, 458 (2007).
[7] T. A. Wesolowski and A. Warshel J. Phys. Chem., **97**, 8050 (1993).
[8] J. W. Kaminski, S. Gusarov, T. A. Wesolowski, and A. Kovalenko, (2009), (submitted).
[9] D. Yokogawa, H. Sato, S. Gusarov, and A. Kovalenko, (2009), (submitted).
[10] T. Luchko, S. Gusarov, D. A. Case, J. Tuszynski, and A. Kovalenko, (2009), (submitted).
[11] A. E. Kobryn and A. Kovalenko, J. Chem. Phys. **129**, 134701 (2008).
[12] A. E. Kobryn and A. Kovalenko, Internat. J. Quantum Chem., **109**, 1666 (2009).

Poster Session I (Wednesday, July 22)

Arranged in alphabetical order

[P1-1]

Ab-initio study on the formation of tri-iodide CT complex from the reaction of iodine with n-electron donors

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In continuation to our previous experimental work, the charge transfer (CT) interaction between iodine and some n-electron donors has been thoroughly investigated via theoretical calculations. A Hartree-Fock, 3-21G level of theory was used to optimize and calculate the Mullican charge distribution scheme as well as the vibrational frequencies of the free donors and its CT complexes with one and two iodine molecules. A very good agreement was found between experiment and theory. New illustrations were concluded with a deep analysis and description for the vibrational frequencies of the formed CT complexes.

[P1-2]

Computational studies on cyclic [n]paraphenyleneacetylenes and cyclic butadiyne-bridge [4n]paracyclophynes using homodesmotic reactions

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Since the discovery of fullerenes, the search for many potentially stable forms of carbon and hydrocarbons which are either polymeric or molecular in nature has been vigorously pursued. Fullerene chemistry and construction of acetylenic-phenyl carbon rings have provided new classes of advanced functional materials for technological applications[1]. Polycyclic hydrocarbons containing phenyl rings connected at the para positions to each other by acetylenic bonds are generally known as cyclic [n]paraphenyleneacetylenes ([n]CPPAs) and butadiyne- bridge [4n] para cylophynes (B-B[4n]PC). In this poster, homodesmotic reaction scheme[2] coupled with density functional theory has been used to estimate theoretically strain energies and heats of formation of [n]CPPAs and B-B[4n]PC. Calculations have been done for a series of [n]CPPAs and B-B[4n]PC containing up to ten phenylacetylene units. Strain energies of [n]CPPAs and B-B[4n]PC decrease while heats of formation increase steadily with increase in the number of phenylacetylene units using homodesmotic reaction schemes. B3LYP[3] and mPW1PW91[4] functionals have been used with the Pople basis set[5] 6-31G* to analyze the trends. The results are sensitive to the scheme of homodesmotic reaction chosen, thereby necessitating careful chemical consideration before spending considerable computational resources for higher [n]CPPAs and B-B[4n]PC not considered here. Computational estimates for the ring diameter of [n]CPPAs and B-B[4n]PC absolute entropy have also been obtained here.

1. Kawase T.; Darabi H. R. *Chem. Rev.* **2006**,*106*, 5250.
2. Wheeler S. E.; Houk K. N.; Schleyer P. R.; Allen W. D. *J. Am. Chem. Soc.* **2009**,131,2547.
3. Becke, A. D. *J. Chem. Phys.* **1993**, *98*,5648.
4. Adamo C.; Barone, V. *J. Chem. Phys.* **1998**, *108*,664.
5. Francl M. M.; Pietro W. J.; Hehre W. J.; Binkley J. S.; Gordon M. S.; Defrees D. J.; Pople J. A. *J. Chem. Phys.* **1982**, *77*,3654.

[P1-3]

Molecular Dynamics Simulations of Protein (HLA-Cw6-B2m-KIR2DS2) Associated with Skin Disease Psoriasis

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Molecular dynamics (MD) simulations were performed to study the structure and dynamics of (HLA-Cw6-B2m-KIR2DS2) complex for better understanding of the skin disease psoriasis. Numerous studies have proved that Cw6 antigens is positively associated with psoriasis[1]. The overall aim of this study is to come up with a new peptide or a small protein therapeutic for psoriasis that is able to disrupt the interaction between HLA-Cw6 and its receptor. This project provides a detailed understanding of the HLA-Cw6-B2m-KIR2DS2 complex, which is not yet known by using MD simulations. Two complexes were constructed from HLA-Cw3-B2m-KIR2DL[2] and HLA-Cw4-B2m-KIR2DL1[3] by superposition and homology modeling using SWISS-MODEL. All MD simulations were performed using the Gromacs package. The OPLS-AA all-atom force field and Gromos96 was used with the SPC (single point charge) water model. The starting structure for all simulations was constructed by homology model from HLA-Cw3-B2m-KIR2DL2. The simulations were performed in triclinic and cubic periodic boundary conditions. The simulations time step was set to a 1.5 fs, and the MD simulation was performed up to 1x107 time steps (15.0ns). The preliminary results, structures and the binding sites of the complex will be presented and discussed.

[1] Szczerkoswska-Dobosz A., Arch. Immunol. Ther. Exp. (2005), 53; 428-433. [2] Boyington, J. C., Motyka, S. A., Schuck, P., Brooks, A. G. & Sun, P. D. (2000). Nature 405, 537-43. [3] Fan, Q. R. & Wiley, D. G. (1999). J. Exp. Med. 190, 113-23.

[P1-4]

Geometrical Similarity of the Disposition of the Electrostatic Potential of Tetrazole and Carboxylic Group at the Root of their Bioisosteric Relationship

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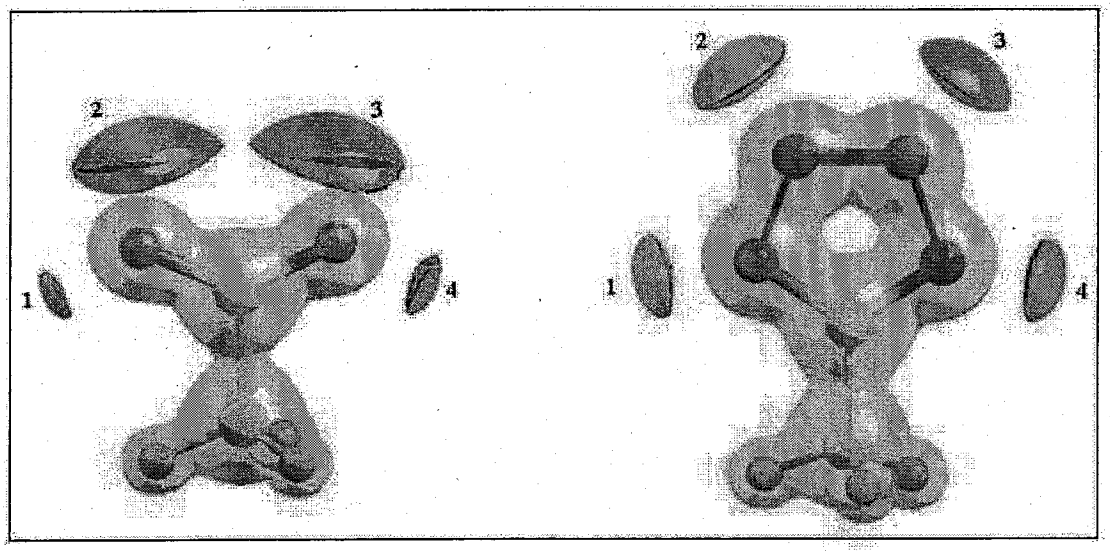
Bioisosterism is the retention of the biochemical and pharmacological properties after the replacement of a certain grouping of atoms in a drug molecule by another grouping. The bioisosteric replacement is often accompanied with some modification of the physicochemical properties, modifications used by drug modellers to optimize the pharmacokinetic and pharmacodynamics properties of the drug.

Tetrazole and carboxylate anions do not have the same number or types of atoms or electrons yet they are known bioisosteres.[1] By the use of the quantum theory of atoms in molecules (QTAIM)[2,3] a remarkable similarity of the average electron density (electron density per unit volume) in the two bioisosteric fragments has been found despite of a lack of similarity in volumes, charges, energies, or electron populations of the bioisosteric fragments capped by a methyl group. It is postulated that the biochemical equivalence of tetrazole and carboxylic acid is due to the similarity of the topography of the electrostatic potential (ESP) (see graph below). The ESP in this case provides a physical basis for the similarity of the two "keys" (the two bioisosteres) that can be complimentary to one and the same "lock" (receptor) composed of four properly oriented positively charged groups.



[1] Herr, R. J. Bioorg. Med. Chem., 2002, 10, 3379-3393.
[2] Bader R.F.W. Atoms in Molecules: A Quantum Theory, Oxford, U.K.(1900).
[3] Matta C.F.; Boyd R.J. (EDs.) The Quantum Theory of Atoms in Molecules: From Solid State to DNA and Drug Design.

[P1-5]

Mechanism of ionic recombination in the system $Cs^+ + Br^- + Xe$

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The main feature of recombination processes is necessity of stabilization of recombining particles via transfer of a part of energy of a formed molecule to the third body. In chemical kinetics three mechanisms of recombination, i.e. stabilization of recombining ion pair (A^+ and B^-) by the third body (C) are considered:

- direct three-body recombination, proceeding in one stage

$$A^+ + B^- + C \rightarrow AB + C \qquad (1)$$

- so-called Lindeman mechanism with a transfer of energy from excited associate to the third body

$$A^+ + B^- \leftrightarrow AB^* \qquad (2a)$$

$$AB^* + C \rightarrow AB + C \qquad (2b)$$

- three-steps mechanism including formation of an intermediate complex of one of ions with the third body and its subsequent reaction with other partner of recombination

$$A^+(B^-) + C \leftrightarrow CA^{+*}(CB^{-*}) \qquad (3a)$$

$$CA^{+*}(CB^{-*}) + C \rightarrow CA^+(CB^-) + C \qquad (3b)$$

$$CA^+(CB^-) + B^-(A^+) \rightarrow AB + C \qquad (3c)$$

Apparently from these schemes, unlike the first mechanism others two are realized through sequence of double collisions. It is obvious that realization of this or that mechanism essentially depends by nature of recombining particles and a stabilizing third body, and also on collision conditions. Properties of particles are shown through interaction potentials between participants of process, and conditions of collisions are defined by their kinematics which includes such parameters as energy of rapprochement of ions, energy of collision of ion pair with the third body and impact parameter of this collision, a collision configuration, etc.

To prefer this or that mechanism on a basis only the kinetic data it is almost impossible. In books and articles on kinetics advantage is given to one of consecutive two-body mechanisms, and the contribution of direct process is considered as neglected small. Such conclusions, as a rule, are results of simple calculation of a parity of number of double and threefold collisions on the basis of rough estimates of the sizes of particles.

Trajectory simulation of dynamics of ionic recombination in system $Cs^+ + Br^- + Xe$ shows, however, that the probability of a direct three-body recombination under identical conditions of collision considerably exceeds corresponding value for two other considered mechanisms. Probability of recombination for Lindeman mechanism assuming a delay of the second stabilizing collision relatively the moment of rapprochement of ion pair, below probability of recombination at simultaneous collision of three particles for any value of this delay. For the third mechanism intermediate complexes $XeCs^+$ and $XeBr^-$ owing to a low bond energy are formed only at energies below 1,0 eV and, for example, at relative energies of particles 0,3 eV the cross sections of formation of these complexes is smaller than cross section of formation of molecule CsBr accordingly in 70 and 250 times.

[P1-6]

Ensemble-based virtual screening reveals novel inhibitors for the MDM2-p53 interaction

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Tumor suppressor p53 is a key regulator of cell cycle, apoptosis, DNA repair and senescence. Because of its vital role as a guardian for the genome, tumor cells have developed numerous ways to disable its function. Indeed, the Tp53 gene is mutated or deleted in ~50% of human cancers. In the rest of human cancers, although p53 retains its wild type, the p53 activity is eradicated by its main cellular inhibitor, murine double minute 2 protein (MDM2). Although MDM2 has no intrinsic enzymatic activity, recent studies proved that activation of the p53 pathway through disrupting its interaction with MDM2 is a promising therapeutic strategy of cancers that retain the wild-type p53. In particular, the last decade has witnessed the finding of an increasing number of non-peptide, small-molecule MDM2 inhibitors with promising binding affinities. Of these molecules only three compounds, namely, Nutlin-3, MI-219 and TDP665759 showed high binding affinity, and desirable pharmacokinetic profiles in cells, however, none of them has been progressed to clinical phase evaluations, fueling enthusiasm for the discovery of new MDM2-inhibitors. We applied the relaxed complex scheme technique to account for the full receptor flexibility in screening for MDM2 inhibitors. In this study, we have filtered the NCI diversity set, DrugBank small-molecules for novel MDM2 inhibitors. In addition, we have appended a diversity set of ~ 3000 similar structures for the three well-studied MDM2 regulators, Nutlins, MI-219 and TDP665759 to the docked compounds. Our results uncovered novel and promising inhibitors for the MDM2-p53 interaction.

[P1-7]

Atomic sizes in terms of physical observables

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We introduce a general definition of the radius of an atom in terms of its ionization energy, I, as derived from a maximal condition applied to the radial distribution function of the spherically-symmetrical electron density. This atomic radius is given by $r_o = a_0 \sqrt{(I_H/I)}$, where I_H is the ionization energy of the hydrogen atom and a_0 is the Bohr radius. The atomic radii exhibit the expected periodic trends, including lanthanide and actinide contractions. Additionally, strong correlations with previously published atomic radii lead us to conclude that we have found a universally valid definition of the atomic radius, given exclusively in terms of an intrinsic property, the ionization energy of an atom, which is equally available from experiments and theoretical computations. An advantage over previous definitions is that this definition provides a complete table of atomic radii for the first 104 elements as given by their respective experimentally-determined ionization energies.

[P1-8]

Molecular dynamics simulation of argon nucleation from supersaturated vapor

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The spontaneous formation of liquid droplets in a supersaturated vapor is the best known example of homogeneous nucleation. In recent years research on gas-liquid nucleation has gained a new impulse. This is partly due to the emergence of experimental techniques that make it possible to measure nucleation rates with high accuracy and produce small clusters of various materials (metals, medicines, etc). The modern theory of interfacial thermodynamics has its origins in the Gibbs theory of surface tension. The key parameter in the Gibbs theory is surface tension attributed to a so-called surface of tension. The critical nucleus is often extremely small in size so that the homogeneous bulk properties are not attained even in its center. As well for small clusters surface tension turns out to be strong function of droplet radius. That's why direct molecular dynamics simulation of nucleation processes in supersaturated vapor is an appealing method for the detailed investigation of the particle growth dynamics and for the validation of existing nucleation theories.

In present research we study the process of nucleation in supersaturated argon vapor. Two kinds of simulations were carried out: in micro canonical NVE and isothermal NVT ensembles. The influence of the size of the simulation system was investigated. For a certain size of a simulation cell, at a given temperature and supersaturation, a dynamic coexistence between states with and without cluster was observed and thoroughly studied. The distribution function of the largest cluster size in such coexistence regime allows us to estimate critical cluster size and reversible work of its formation.

[P1-9]

SA-CASSCF and R-matrix calculations of low-energy electron collisions with uracil

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A series of R-matrix calculations [1] within the static exchange, static exchange plus polarisation and close-coupling approximation on electron-uracil collisions are presented [3]. Of particular interest in this system is the presence of the low-energy quasibound states of the compound system as such resonances are thought to be the key initial process in the radiation damage of living systems [2]. Particularly as input for the close-coupling calculations, a series of target calculations are performed which consider low-lying singlet and triplet excited states of the uracil target. Here the (14,10) active space and associated State-Averaged Complete Active Space Self Consistent Field [4] orbitals were used.

References

[1] L. A. Morgan, J. Tennyson, C. J. Gillan, Computer Phys. Comms. 114, 120, (1998).
[2] B. Boudaiffa, P. Cloutier, D. Hunting, M. A. Huels, L. Sanche, Science 287, 1658 (2000).
[3] A. Dora, J. Tennyson, L. Bryjko, T. van Mourik, J. Chem. Phys., submitted.
[4] B.O. Roos, Adv. Chem. Phys. 69, 339 (1987).

[P1-10]

Computational Study of the [1,4] Sigmatropic Shift

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Very few discussions have been given in the literature for [1,4]-sigmatropic rearrangements, which are the heteroatomic-analog of the [1,5] rearrangements in conjugated systems. Yet, the [1,4] shift is common for systems whereby two atoms of a double bond in a conjugated system are replaced by one atom with a lone pair. The usual replacement atom, X: is N, O, or S, but may also be a C anion. One reason for the rare occurance of [1,4]-shifts in the literature may be that they occur mainly in short lived intermediates such as ylides and 1,3-dipoles and are not as evident as [1,5]-C shifts between stable precursors. The present is a DFT computational study of [1,4] shifts in mono- and bicyclic compounds. The shifts occur between 1,3-dipoles and the more stable ene-amine. The applicability of the Hammond Postulate and agreement between calculated and experimental Hammett values are demonstrated.

[P1-11]

A theoretical investigation on the possible mechanism of UROD

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UROD is a key enzyme in the synthesis of tetra-pyrrole rings thus playing an essential role in the formation of the heme prosthetic group.[1] Hence, there is tremendous interest in understanding the biochemistry of UROD, in particular the enzymatic mechanism by which it decarboxylates its substrate (uroporphyrinogen III) to give corproporphyrinogen III. Current experimental evidence suggests that the reaction occurs within a single active site that contains several invariant amino acid residues.[2,3] However, the exact role of these invariant residues is currently debated and consequently several mechanisms have been proposed. In our investigation, various computational methods have been used to investigate the enzymatic mechanism of UROD. More specifically, a molecular mechanics based docking method was used to determine the most probable initial binding conformations of uroporphyrinogen III within the active site thus allowing a molecular dynamics simulation to allow each of the systems to reach an equilibrium conformation. From this, a quantum mechanics/molecular mechanics study was performed on large active site models of the various systems to determine the energy changes and conformational and/or configurational changes within the active site during the course of the reaction. Some results will be presented. [1]Phillips, J. D. et. al, EMBO J. 2003, 22, 6225.[2]Akhtar, M., Ciba Found. Symp. 1994, 180, 131.[3]de Verneuil, H., J. Biol. Chem. 1983, 258, 2454

[P1-12]

Virtual Screening of the Protein Data Bank: Searching for Sites with Pre-defined Chemistry

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A computational approach was developed to search the Protein Data Bank (PDB) and identify potential binding pockets possessing pre-defined chemistry. This method, which was implemented using the ICM software (Molsoft L.L.C.), can be broken down into three distinct steps: First, the target receptor chemistry must be defined, and a pharmacophore is used to represent the desired chemical and structural features of the pocket. In a separate step, putative binding sites are extracted from the PDB and stored in a large SD file, yielding a focused library of protein pockets. Finally, the pharmacophore is used as a query to screen the virtual library of pockets, and select sites matching the desired chemistry and geometry. As an example, we show how this approach has been used to screen the PDB for sites having a similar chemistry to sites that bind methyl-lysine marks on histone tails. Results demonstrate that most known Me-Lys binding pockets are retrieved using this technique, and that novel sites with similar chemistry can be identified.

[P1-13]

Chirality transfer at chiral stationary phases: Insights from simulations

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Chiral stationary phases are invaluable tools for the chromatographic separation of enantiomers. Despite their importance, interfacial characteristics and selective mechanisms are often poorly understood. Results from molecular dynamics simulations of three commercially-available chiral stationary phases will be presented: dinitrobenzoyl derivatives of phenylglycine and leucine, and Whelk-O1, a particularly successful brush-type selective compound. Modelling of the solvated chiral interfaces provides the basis for an analysis of the selective surfaces. Solvation of the chiral selectors will be examined with an emphasis on chirality transfer from the interface to nearby solvent molecules. Interfacial chirality transfer will be compared to transfers from solutes in the bulk.

[P1-14]

Ab-initio potential energy and dipole moment surfaces for CS_2: Towards an optimal control of a CARS process using the OCT-MCTDH approach

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We have obtained CASPT2/C:VTZ, S:aug-cc-pV(T+d)Z ground state potential energy and dipole moment surfaces for CS_2. Using the potential energy surface (PES), we have calculated vibrational energies and the corresponding vibrational wave functions using the multi-configuration time-dependent Hartree (MCTDH) approach (1). These results are compared to experimental and previous theoretical data in order to assess the accuracy of the PES. In the future, the surfaces will be used for the study of a coherent anti-Stokes Raman (CARS) process which selectively excites or suppresses molecular vibrational modes of CS_2 in the gas phase, as observed experimentally (1). Together with an optimal control theory (OCT) implementation within MCTDH, developed by some of us (M.S. and A.B.) (3), and the experimental laser pulses (supplied by the authors of Ref. 1), we want to investigate questions such as the mechanism and the role of the intermolecular processes in the control of the molecular modes.

1) G. A. Worth, M. H. Beck, A. Jaeckle, and H.-D. Meyer. The MCTDH Package, Version 8.2, (2000), University of Heidelberg, Heidelberg, Germany. H.-D. Meyer, Version 8.3 (2002), Version 8.4 (2007). See http://mctdh.uni-hd.de

2) A. Scaria, J. Konradi, V. Namboodiri and A. Materny. J. Raman Spectrosc. 2008; 39: 739 - 749

3) M. Schroeder; J.-L. Carreon-Macedo; A. Brown. Physical Chemistry Chemical Physics, 2008, 10: 850-856.

[P1-15]

Reverse transcriptase resistance to NRTIs: PPi leaving is coupled to fingers domain opening

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Reverse transcriptase (RT) is the HIV enzyme that converts the single stranded RNA from the virus into double-stranded DNA that can be incorporated into the host cell genome. Due to its essential role in HIV replication, RT is a suitable target for antiretroviral therapy. Accordantly, several RT inhibitors are currently used in the clinic. The first to be synthesized were competitive inhibitors called nucleoside reverse transcriptase inhibitors (NRTIs). During DNA synthesis by RT, the NRTI/substrate first binds to the N site of the enzyme promoting the fingers domain closing conformational change. Then, the 3'OH of the DNA strand attacks the α phosphate of the NRTI/substrate. The N site contains two magnesium ions that are very important for the reaction (metal A and B). Studies on DNA/RNA enzymes suggested that the role of metal A was to assist in the nucleophilic attack and that metal B stabilized the leaving group [1]. After incorporation the PPi leaves the active site. The fingers domain should then open and RT translocates one base pair to add the next substrate. The enzyme and incorporated inhibitor are unable to add the next nucleotide. The treatments with the inhibitors fail due to the high rate of viral mutation which leads to resistance at incorporation or afterwards by excision (promoted by ATP) [2].

We found, by performing molecular dynamics simulations of RT with a normal substrate and with the inhibitors AZT and d4T, different patterns of interactions of the active site residues for the complex with the normal substrate in relation to the complexes with the inhibitors. In the complex with the normal substrate, the fingertip residues establish interactions mainly with the leaving group, PPi, which is also stabilized by metal B. On the other hand, in the complexes with the inhibitors, the fingertip residues establish interactions mainly with the inhibitors. We proposed that for the normal substrate pyrophosphate leaving was coupled to fingers domain opening. For the inhibitors, pyrophosphate leaving was uncoupled from fingers domain opening and hence ATP could bind to the closed RT conformation promoting excision [3,4].

1) W. Yang, J. Y. Lee and M. Nowotny, Making and breaking nucleic acids: Two-Mg2+-ion catalysis and substrate specificity. Molecular Cell, 22, 5-13 (2006).

2) A. T. P. Carvalho, P. A. Fernandes and M. J. Ramos, Molecular insights into the mechanisms of HIV-1 reverse transcriptase resistance to nucleoside analogs. Mini-Reviews in Medicinal Chemistry, 6, 549-555 (2006).

3) A. T. P. Carvalho, P. A. Fernandes and M. J. Ramos, Insights on resistance to reverse transcriptase: The different patterns of interaction of the nucleoside reverse transcriptase inhibitors in the deoxyribonucleotide triphosphate binding site relative to the normal substrate. Journal of Medicinal Chemistry, 49, 7675-7682 (2006).

4) A. T. P. Carvalho, P. A. Fernandes and M. J. Ramos, The excision mechanism in reverse transcriptase: Pyrophosphate leaving and fingers opening are uncoupled events with the analogues AZT and d4T. Journal of Physical Chemistry B, 111, 12032-12039 (2007).

[P1-16]

Amphiphilic Alternating Copolymer Nanoarchitectures: The Characterization of Poly(Isobutylene-alt-maleic acid)

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Amphiphilic copolymers nanostructures have proven very efficient for the solubilization of small hydrophobic molecules in water for applications in storage, delivery and nanoelectronics. Alternating copolymers are expected to show significant advantages over other self-assembled structures due to uniform interactions along the copolymer chain. However, the association and properties of self-assembled nanoarchitectures composed of such copolymers are still not well understood. The amphiphilic copolymers are composed of a pH sensitive hydrophilic group, maleic anhydride alternating and of a hydrophobic group. Our research focuses on the characterization of poly(isobutylene-alt maleic anhydride)'s (IMA) association in water and of the influence of different hydrophobic interactions during the self-assembly process. A theoretical approach is chosen to investigate and characterize the behaviour of IMA chains at different pH values (3, 7 and 12). The self-assembly was characterized using several structural modeling methods from molecular mechanics to *ab initio*. The second part of the study involves the application of these nanoarchitectures to synthesize polypyrrole nanowires. The interaction of pyrrole and the copolymer template was analysis using DFT molecular modeling theory. The theoretical predictions are compared to experiment.

[P1-17]

First Principles Modeling of the Lithiation of Silicon

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Silicon has emerged as an excellent candidate negative electrode material for Li-ion batteries over the last several years. It offers excellent specific capacity, volumetric energy density, and thermal stability compared to graphite, the common commercial negative electrode material. When Li is added to small particles of Si (less than 500 nm) in an electrochemical cell at room temperature, the Si becomes amorphous *a*-Li_xSi. When Li is removed from the *a*-Li_xSi, amorphous Si is obtained. However, if lithiation occurs at high temperature (415 °C), the measured potential-composition profile displays plateaus at compositions corresponding to the crystalline phases: $Li_{12}Si_7$, Li_7Si_3, $Li_{13}Si_4$, $Li_{22}Si_5$. Density functional theory (DFT) total energy calculations, are performed to accurately reproduce the potential-composition curve of Li/Li_xSi electrochemical cells at high temperature using the experimentally observed crystalline phases. A protocol is proposed to extend the use of DFT to model the lithiation of Si at room temperature through incremental lithiation. Potential-composition curves obtained with this protocol are compared with experiment and found to be in good agreement. Radial distribution functions are also calculated and presented.

[P1-18]

A Computational Study of Stacking and T-shaped Interactions of the DNA Nucleobases with Protonated or Neutral Histidine

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As our understanding of biological processes increases, the importance of noncovalent interactions is becoming clear. For example, noncovalent interactions between the natural nucleobases are instrumental for the formation of the DNA double helix. Interactions between DNA and proteins are also extremely critical for a variety of different events in nature, as well as for the development of pharmaceuticals and biochemical techniques. Although hydrogen-bonding interactions between biomolecules are well understood, many questions surround other noncovalent interactions such as stacking (π–π) and T-shaped (X–H•••π or lone-pair•••π) contacts. Computational chemistry is an ideal tool to study such interactions compared with experiment, where it is difficult to separate the total stability of biological complexes into discrete interactions.

The present poster will report on computational studies of π–π and X–H•••π interactions between the natural DNA nucleobases and neutral or protonated histidine. Although interactions involving neutral histidine were previously studied in the Wetmore group, histidine exists in a protonated form in many enzymatic environments. Furthermore, cation-π interactions involving protonated histidine may have quite different propπ–π interactions involving neutral histidine. This poster reveals these differences, as well as the magnitude of these interactions, and discusses their biological implications.

[P1-19]

Molecular simulations of fragmentation processes in nano-clusters in the presence of charged macromolecules.

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Composition and properties of highly charged droplets are subjects of active research due to their importance in electrospray techniques coupled to mass spectrometry used in analytical chemistry. Fragmentation mechanism of the charged droplets is believed to play a key role in determining the final charged state of the sample. To explain the fragmentation mechanism in electrospray,Rayleigh's model is widely used as the theoretical basis for modelling the stability of highly charged liquid droplets. In an intuitive manner the model considers a conducting sphere with uniform distribution of charges on its surface. The electrostatic and surface terms are expanded in terms of the spherical shape and small fluctuations from the sphere keeping the volume constant. We performed simulations of clusters composed of water molecules and simple ions of the same sign and we found that Rayleigh's model was obeyed even for the cases of systems of few hundreds water molecules. In the study we introduced a new reaction coordinate and we were able to study the activated character of the process below the Rayleigh limit. In the next step we introduced macroions instead of simple ions and we found that the assumptions of Rayleigh's model break down. This has implications in the way that the fragmentation mechanism is explained in electrospray experiments. The simulation findings of the fragmentation mechanism in the presence of macroions as well as the implications in the electrospray mechanisms will be presented.

[P1-20]

Computational Determination of Putative Binding Sites of Anesthetics to the Cytoskeleton

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The cytoskeleton is essential to cell morphology, cargo trafficking, and cell division. As the neuronal cytoskeleton is extremely complex, it is no wonder that a startling number of neurodevelopmental, neurological, and neuropsychiatric disorders (including Alzheimer's Disease, Frontotemporal Dementia, and Bipolar Disorder) share the feature of a dysfunctional cytoskeleton. Recent concern has been raised about the possible link between anesthesia and the exacerbation of neurodegenerative disorders. It is known that the presence of anesthetics affects microtubules, with exact mechanisms yet to be identified. As such, the interaction of anesthetics with tubulin was investigated. NAMD based molecular dynamics simulations, followed by Autodock based free energy calculations and surface geometry techniques were used to determine putative binding sites for halothane, and the halogenated ethers. Locations of the putative binding sites, and the relation to cytoskeleton function are presented.

[P1-21]

Alternative Ornstein-Zernike Models for the Homogeneous Electron Liquid

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Alternatives to the conventional Ornstein-Zernike direct correlation function (DCF) are proposed, and applied to the homogeneous electron liquid. This generalizes the recent work of Amovilli and March [Phys. Rev. B 76, 195104 (2007)], where the ordinary Ornstein-Zernike DCF was used. Unlike the conventional Ornstein-Zernike DCF, the alternative DCFs do not conflict with normalized exchange-correlation holes.

[P1-22]

QM/MM Simulations and High-throughput Virtual Screening on UDP-Sugar Hydrolases from the Pseudaminic Acid Biosynthetic Pathway

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Flagella of the bacteria *Helicobacter pylori* and *Campylobacter jejuni* are important virulence determinants, whose proper assembly and function is dependent upon glycosylation at multiple positions by sialic acid-like sugars, such as 5,7-diacetamido-3,5,7,9-tetradeoxy-L-glycero-L-manno-nonulosonic acid (pseudaminic acid). The second and the fourth enzymatic steps in the pseudaminic acid pathway are performed by the nucleotide-sugar hydrolase PseB and PseG, respectively. In order to identify and design novel antimicrobial molecules which are specific for the virulence factors from the bacterial pathogens, we performed molecular modeling and high-throughput virtual screening on PseB and PseG.

High resolution crystal structures of *C. jejuni* PseG in apo form and as a complex with its UDP product have been determined. However, the PseG-substrate complex structure has not been determined yet. In order to better understand the molecular basis of the PseG catalytic reaction, we performed molecular modeling at the QM/MM level to suggest a most likely PseG-substrate complex structure. Starting from a Monte-Carlo-Minimization sampled conformation of the UDP-substrate, we performed 3 ns classical MD simulation, followed by 120 ps QM/MM simulation, where the entire substrate molecule was included in the QM region described with the semi-empirical PM3 Hamiltonia, while the solvated protein was treated at the molecular mechanics level using the AMBER force field. Our modeling identifies a water molecule coordinated by His17 as the putative nucleophile and suggests the UDP-sugar substrate adopts a twist-boat conformation upon binding to PseG, enhancing the exposure of the anomeric bond cleaved and favoring inversion at C1.

We have developed a high-throughput virtual screening pipeline by combining our fast exhaustive docking program and the solvated interaction energy (SIE) scoring function with MD simulations. Using this pipeline, we screened 1.6 million drug-like compounds from the ZINC library, against the PseB and PseG targets, respectively. We have identified number of virtual hits for the two targets. Some of the hits have been confirmed by *in vitro* validation experiments.

[P1-23]

Many Body Perturbation Methods Implemented into a Diatomics in Molecules Hamiltonian

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Recently we have shown how an approximate diatomics in molecules (DIM) Hamiltonian in which all three- and four centered two-electron integrals vanish can be used to capture the nondynamic electron correlation in methods such as generalized valence bond theory with little loss in accuracy compared to the exact result but at a fraction of the computational cost. In this poster we examine the use of this Hamiltonian for capturing the dynamic electron correlation. Because this Hamiltonian has an orthonormal atomic orbital basis and one/two centered integrals a transformation into a basis of strictly localized bonds, antibonds and hybrid atomic orbitals can be rapidly performed. Starting with a reference state of doubly occupied strictly localized bonds a localized perturbation treatment is carried out. Results on moderately large molecular systems are presented and compared with exact calculations for accuracy as well as computational timings.

[P1-24]

The Classical-Map Hyper-Netted-Chain (CHNC) technique for inhomogeneous electron systems- an order-zero method.

Application to quantum dots.

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An approximate method which represents an interacting Fermi liquid at zero temperature by an "equivalent" classical Coulomb fluid at finite temperature is studied here in the context of an inhomogeneous electron distribution in a "quantum dot, i.e.,in a 2-D harmonic confining potential. The use of such classical maps, together with methods of classical statistical mechanics to deal with the many-body problem had been demonstrated in previous work via applications to 2-D and 3-D electron fluids as well as hydrogen plasmas. Such methods work directly with the charge distribution and do not need basis sets, matrix-element evaluations etc.,and form a class of "order-zero" methods which are independent of the number N_e of electrons treated. Thus calculations for thousands of electrons are no more difficult than for a few electrons. The calculation yields spin-dependent pair-distribution functions and energies. The many-body problem is classical, and exchange appears via an effective potential which reproduces the Fermi hole in the parallel-spin pair-distribution functions. The classical many-body problem was handled using the hyper-netted-chain (HNC) integral equations. In this study we make a fairly detailed comparison of the results from such a Classical-map Hyper-Netted-Chain (CHNC) technique, with those from a well established microscopic calculation using standard density-functional theory and Quantum Monte carlo. These results show that while a result to within a few percent accuracy can be easily obtained using CHNC, more accurate results require a better formulation of the correlation potential.

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Phsy. Rev. Let. **84**, 959 (2000)

[P1-25]

Electronic Couplings between Charge-transfer States and Excitons in Organic Photovoltaics

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An *ab inito* density functional theory (DFT) based method is presented for computing electronic couplings between charge-transfer (CT) states and excitons in organic molecules. We demonstrate this method by computing electronic couplings in a photovoltaically relevant organic dimer. The resulting coupling magnitudes provide insight into the transition rates between the dimer's electronic states. In addition, we use the computed couplings together with the diabatic-like DFT states to compute adiabatic states. The resulting transition rates and adiabatic states allow us to study the electronic pathways that lead to current generation in organic photovoltaic devices.

[P1-26]

Glutathione transferase: GSH activation mechanism proposal

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The cell detoxification mechanism of xenobiotic and endobiotic compounds follows a series of different steps. To begin with, toxic compounds are converted into strong electrophiles, by the mixed-function oxidation activity of cytochrome P-450. Those electrophiles are subsequently transformed into more soluble and less toxic substrates, by conjugation with glutathione (GSH) due to the catalytic activity of Glutathione transferases (GSTs), which are recognized by ATP-dependent transmembrane pumps such as P-glicoproteins and MRP family proteins, and consequently expelled from the cell. GSTs studies are of great importance since they have been implicated in the development of drug resistance in tumoral cells and are related to human diseases such as Parkinson's, Alzheimer's, atherosclerois, liver cirrhosis, aging and cataract formation. In terms of structure GSTs can be homodimers or heterodimers having each monomer two active centers, a G-site pocket for glutathione (GSH) and an H-site pocket for the electrophilic substrate. When GSH binds to the G-site, the pKa of its thiol group drops 1.5 units promoting its deprotonation. This strong nucleophilic thiolate is now able to react with the electrophilic substrate, bounded in the H-site, building up a more soluble and less toxic compound. The nature of the residue that, behaving as a base, deprotonates the GSH thiol group is still unknown.

Based on QM/MM calculations we propose a mechanism for GSH activation with an overall free energy barrier consistent with the enzyme kinetics experimental studies.

D. F. Dourado, P. A. Fernandes, B. Mannervik and M. J. Ramos, Chemistry 2008, 14, 9591-9598

[P1-27]

Perturbation Theory in the Space of Variationally Fitted Kohn-Sham Potentials

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Variational fitting allows perturbation theory to be formulated completely in terms of the fitted Kohn-Sham potential, which is called the Sambe-Felton (SF) potential. Using the finite Gaussian basis sets of molecular quantum chemistry, there is a one-to-one correspondence between Roothaan molecular orbitals and SF potentials. The finite, order-N^2, where N is the number of atoms, set of linear-combination of atomic orbitals (LCAO) molecular orbital coefficients is completely determined by the order-N linear-combination of atomic potentials (LCAP) coefficients. Variational fitting can be applied exactly as it is in the self-consistent-field (SCF) case to each of the even-orders of perturbation theory [1]. Thus, for example, hardness and hyperhardness–second and third derivatives of the energy with respect to orbital occupation numbers–are computed to precisely machine precision in V-representable perturbation theory for Becke's standard set of 56 molecules [2]. The Hohenberg-Kohn theorem suggests a formulation of SCF-solution stability analysis in the space of SF potentials.

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[1] B. I. Dunlap, Phys. Rev. A 76, 062512 (2007).
[2] B. I. Dunlap, J. Chem. Phys. 129, 244109 (2008).

[P1-28]

Ab initio Alkyl Ions: Open and Closed (PCP^+) Structures

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Branching and beta-scission mechanisms of alkyl carbocations are fraught with the problem of the relative importance of "closed" (nonclassical) versus "open" (classical) structures. Closed structures have been variously described as protonated-cyclopropane (PCP^+) or alkyl-bridged; open structures would include classical carbocations and H-bridged ones. We have performed QCISD(T)/cc-pVTZ single-point calculations and QCISD/cc-pVDZ geometry optimizations for 26 structures of open and closed forms of hexyl ions. Single point energy calculations were made prior to running the optimization files in order to have estimates of relative energies of unstable (nonstationary) structures. The results show that secondary hexyl ions prefer closed structures whereas the tertiary hexyl ions prefer the open forms. The primary hexyl ions for both the closed and open forms undergo alkyl shifts to form open-form tertiary ions. We use this data to present a mechanism for 1,1,2-trimethylPCP^+ and 1,2,3-trimethylPCP^+ rearrangements, which we suspect is at the core of the mechanisms of branching and cracking of alkyl ions.

[P1-29]

Entropy Contributions in pKa Computation: Application to Alkanolamines and Piperazines

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The pKa values of 17 amines, alkanolamines, and piperazines have been computed using quantum chemistry techniques and the IEFPCM continuum solvation model. Several techniques were tested, including B3LYP and MP2 levels of electronic structure theory, the addition of an explicit water molecule inside the continuum cavity, and special scaling of cavity radii for ions. Proper entropy corrections, often neglected in pKa studies, are discussed and utilized. The use of explicit water inside the cavities reduced the pKa rms error by 34%. As noted several years ago, ringed compounds do seem to be pathological cases for continuum solvation models, and the use of a second fitting parameter for these compounds dramatically lowered the overall rms error a further 42-45%, to below 0.9. Our best procedure reduces the errors found in a previous technique for similar compounds by 57%.

[P1-30]

Is the Condensed Fukui Function Negative in Charge Disproportionation Compounds?

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This work is focused on studying charge disproportionation compounds (CDC) by means of the Fukui Fuction, within the framework of Density Functional Theory of chemical reactivity. CDC's have an exotic redox chemistry, where oxidation (reduction) of the entire molecule is coupled to reduction (oxidation) of one of the atoms (or ligands) therein. Negative values of the condensed Fukui Function could be associated with such chemical behaviour, pointing out the sites where the electron density would decrease (increase) when an electron is added to (removed from) the molecule. Dinuclear metal complexes are good candidates for CDC's: their disproportionation behaviour would involve a change in the number of occupied orbitals on the metal centers and an increase in spin-multiplicity. In particular, we study dicobalt complexes bridged by a 1,4dichlorotetraoxolate ligand (dCht) [TPyACo(II)$dCht_{(2-)}$Co(II)TPyA]$(BF_4)_2$, [TPyA: tris(2-pyridylmethyl)amine], which have been experimentaly characterized as CDC's.

Ayers,P.W.; Phys.Chem.Chem.Phys., 2006, 8, 3387-3390.
Miller,J.S. and Min,K.S.; Angew.Chem.Int.Ed. 2009, 48, 262–272

[P1-31]

Why do α,β-Unsaturated and Saturated derivatives of Mg and Ca behave as Metal Acids in the Gas Phase?

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The gas-phase acidity of R-XH (R = H, CH3, CH2CH3, CHCH2, CCH) alkaline-earth derivatives (X = Be, Mg, Ca) has been investigated through the use of high-level CCSD(T) calculations using a 6-311+G(3df,2p) basis set. BeH2, is a stronger acids than BH3 and CH4, for two concomitant reasons: a) the dissociation energy of the Be-H bond is smaller than the dissociation energies of the B-H and C-H bonds, and b) the electron affinity of BeH• is larger, in absolute value than those of BH2• and CH3•. The acidity increases on going from BeH2 to MgH2 due to these two same factors. Quite importantly, in spite of the fact that the X-H bonds in the R-XH (X = Mg, Ca) derivatives exhibit the expected X+δ-H-δ polarity, they behave as metal acids in the gas phase, and only Be derivatives behave as carbon acids in the gas phase. The Be ethyl derivative exhibits an unexpected high acidity with respect to the methyl derivative, because the deprotonation of the system is accompanied by a cyclization which stabilizes the anion. Similarly to what was for similar derivatives containing heteroatoms from the groups 14, 15 and 16 (Refs. [1], [2], [3], [4]), the unsaturated compounds are stronger acids than the saturated counterparts, with the only exception of the Ca vinyl derivative, which is predicted to be a weaker acid than the ethyl derivative, due to an extra-stabilization of the neutral form. Most importantly, among ethyl, vinyl and ethynyl derivatives, those containing Be, Mg and Ca as heteroatoms are among the strongest gas-phase acids of the periodic table.

References

[1]Mó, O.; Yáñez, M.; Decouzon, M.; Gal, J.-F.; Maria, P.-C.; Guillemin, J.-C. J. Am. Chem. Soc. 1999, 121, 4653.

[2]Guillemin, J.-C.; Decouzon, M.; Maria, P.-C.; Gal, J.-F.; Mó, O.; Yáñez, M. J. Phys. Chem. A 1997, 101, 9525.

[3]Gal, J.-F.; Decouzon, M.; Maria, P.-C.; González, A. I.; Mó, O.; Yáñez, M.; El Chaouch, S.; Guillemin, J.-C. J. Am. Chem. Soc. 2001, 123, 6353.

[4]Guillemin, J. C.; Riague, E. H.; Gal, J. F.; Maria, P. C.; Mó, O.; Yáñez., M. Chem. Eur. J. 2005, 11, 2145.

[P1-32]

Elucidation of the mechanism of Porphobilinogene synthase

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5-aminolevulinic acid (5ALA) and derivates thereof are widely used as prodrugs in photodynamic therapy (PDT). The 5ALA derivates are metabolized into the photosensitizer protoporphyrin IX (PpIX) in the heme biosynthesis. Computational studies have been made on different 5ALA derivates to increase the permeability and yield of PpIX[1-3]. In this study we focus on the heme enzyme porphobilinogene synthase (PBGS), which is catalyzing the asymmetric condensation of 2 5ALA molecules into a porphobilinogene molecule[4].The PBGS catalyzed reaction has an advanced mechanism involving two lysine Schiff bases and a catalytic zinc ion. We elucidate the mechanism using MM, QM and QM/MM methods. MM calculations were performed with the program package Molecular Operation Environment[5] (MOE2008.09). For DFT and QM/MM methods Gaussian03 programme[6] was used.

(1) E Erdtman, DJVA dos Santos, L Löfgren, LA Eriksson: Modelling the behavior of 5-aminolevulinic acid and its alkyl esters in a lipid bilayer. Chemical Physics Letters 463 (2008) 178-82.
(2) E Erdtman, LA Eriksson: Theoretical study of 5-aminolevulinic acid (5ALA) and some pharmaceutically important derivatives. Chemical Physics Letters 434 (2007) 101-06.
(3) E Erdtman, LA Eriksson: Theoretical Study of 5-Aminolevulinic Acid Tautomerization: A Novel Self-Catalyzed Mechanism. J. Phys. Chem. A 112 (2008) 4367-74.
(4) E Erdtman, E Bushnell, J Gauld, LA Eriksson, 2009 To be published
(5) Molecular Operating Environment (MOE). Chemical Computing Group, Montreal, Canada, 2005.
(6) MJ Frisch et al., Gaussian 03, Gaussian, Inc., Pittsburgh PA, 2003.

[P1-33]

An Ab Initio Molecular Orbital Study of the Complexes Formed Between Silicon Tetrafluoride and Some Lewis Bases

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The structures, interaction energies and vibrational spectra of the electron donor-acceptor complexes formed between silicon tetrafluoride and the common Lewis bases ammonia, water, phosphine and hydrogen sulphide have been determined by means of a series of ab initio molecular orbital calculations. The results confirm the trends observed in our previous studies of the complexes formed between the same four bases and the Lewis acids boron trifluoride and sulphur dioxide. The analogous complexes of silicon tetrafluoride with hydrogen fluoride and hydrogen chloride were also examined and, consistent with our earlier findings concerning the adducts of boron trifluoride and sulphur dioxide with these two diatomic species, were found to be very weakly bound, if at all. The trends observed among the properties of all three families are compared.

[P1-34]

Gold cluster stability effects on the localized spin density at the possible sites of chemisorption

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We studied the spin, and charge distributions in nanosystems that resulted from the initial chemisorption of just one α-helix thio-polypeptide of high dipolar moment (35 debye) on two gold cluster surfaces when sulfur was the linking atom. Such a pair of a disk-shaped fifty-one atoms gold cluster (A cluster) and a rod-shaped fifty-five atoms gold cluster (B cluster) was considered. Three and seven chemisorption sites were studied for the clusters A and B respectively. Such special surface sites were classified as central and border positions. Configurations of special interest were selected after as placing the negative or positive end tip of the chemisorbed α-helix molecule pointing almost perpendicular to the gold cluster surface that resulted from cutting a (111) face-centered-cubic crystal. The spin and charge densities calculations for all spin polarized and spin non-polarized singlet states were performed using the electronic density functional theory with a hybrid functional method. The description of the electronic structure was helped using the stability matrices. For both clusters the spin density magnitude found at border positions was always greater than the one at the central positions. A trend of greater total spin density with greater cluster instability was observed. The highest induced spin density by chemisorption was found localized at central positions.

[P1-35]

Structure and properties of peloruside A: Towards understanding of anti-cancer activity

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Peloruside A[1] is a potential candidate for cancer therapy. To understand this anti-cancer drug, we need to investigate the molecular structure and properties of peloruside A. Molecular Dynamics (MD) simulations with isolated peloruside A were performed using the Amber force field and Quantum Mechanics/Molecular Mechanics (QM/MM) approach. QM/MM studies were performed on peloruside A ligand and tubulin protein. The interactions of the ligand and protein were studied along with several analogs of the peloruside ligand; the binding affinities of the interaction of ligand and protein were analyzed.

1. T. Gaitanos, R. Buey et al, Cancer Research 64 (2004), 5063-5067.

[P1-36]

Normal mode calculations with the QM/MM full Hessian and the Mobile Block Hessian (MBH) method

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We have implemented the full Hessian evaluation in QM/MM simulations, as well as the approximate Mobile Block Hessian (MBH). The Hessian is the *3Nx3N* matrix containing the second derivatives of the potential energy surface with respect to the *3N* nuclear coordinates, and needs to be diagonalized when calculating the frequencies and normal modes. In extended systems, however, its calculation, storage and diagonalization is an expensive computational task. Note that even in case of a small QM region, the numerous derivatives of the QM/MM interaction terms still form a bottleneck in the frequency calculation.

Recently, the Mobile Block Hessian (MBH) method was developed in order to reduce the dimensionality of the Hessian. The main concept is the introduction of blocks, which move as rigid bodies during the vibrational analysis. The blocks can also be linear or have atoms in common (leading to adjoined blocks). This block concept is now combined with the QM/MM scheme. The reduced computational cost opens the path to a broad range of applications of normal mode analysis.

[P1-37]

Self-Organizing Map Analysis of Protein Conformational Distributions: Discrimination between Induced Fit and Conformational Isomerism for an Intrinsically Flexible Binding Site

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Protein binding sites are frequently observed to undergo conformational changes upon complexation with their binding partners. This contravention of the rigid lock-and-key mechanism of binding is explained by either 'induced fit' or 'conformational isomerism'. In the former, interactions between the protein and its ligand create a novel minimum in the potential energy surface; in the latter, the ligand preferentially binds to one of a number of pre-existing conformations explored by the unbound protein. Here, we use a Kohonen Self-Organizing Map to analyze conformational distributions obtained by Monte Carlo simulations of a model antibody binding site, both in the presence and absence of its antigenic partner. We show that discrimination can be obtained between induced fit and conformational isomerism for this model system. In addition, the specific antigen-antibody interactions responsible for the observed conformational change within the binding site are elucidated.

[P1-38]

Modelling correlation effects in molecular electronics devices

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Understanding electron transport through molecular electronic devices (MEDs) is essential for the conception of new types of electronic components such as single-molecule transistors. Presently, almost all computational tools used to model MEDs are based on effective one-electron theories. With these models, however, it is not possible to properly account for electron correlation effects.

We present a theory[1] for the inclusion of electron interaction effects in the description of MEDs. Starting from the Hubbard Hamiltonian, we describe a many-electron extension of the Source-Sink Potential (SSP)[2] method. This enables us to study systems in which electron interaction is an important factor. We investigate what impact electron correlation has on various recently discussed phenomena: interference effects in cross-conjugated chains[3] and in aromatic cycles[4-5] such as benzene.

[1] A. Goker, F. Goyer and M. Ernzerhof, *J. Chem. Phys* **129**, 194901 (2008).
[2] F. Goyer, M. Ernzerhof, and M. Zhuang, *J. Chem. Phys* **126**, 144104 (2007).
[3] G.C. Solomon, D.Q. Andrews, RH. Goldsmith, et *al.*, *J. Am. Chem. Soc.* **130**, 17301 (2008).
[4] D.M. Cardamone, C.A. Stafford and S. Mazumdar, *Nano Lett.* **6**(11), 2422 (2006).
[5] M. Ernzerhof, H. Bahmann, F. Goyer, M. Zhuang, R. Rocheleau, *JCTC* **2**(5); 1291 (2006)

[P1-39]

Predicting Proton Exchange Membrane Fuel Cell Platinum Catalyst Durability and Activity using Density Functional Theory

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Platinum still remains one of the most effective catalysts for the Hydrogen evolution reaction (HER) and the Oxygen reduction reaction (ORR) for proton exchange membrane fuel cells. It has been previously shown that Nitrogen doping of a Carbon catalyst support increases the durability and activity of the Platinum. This work uses density functional theory to quantitatively characterize the effects of Nitrogen doping on graphene and single walled carbon nanotubes (SWCNT) as a Pt catalyst support. The graphene systems were evaluated using Lanl2DZ/B3LYP while the SWCNTs were evaluated using Lanl2MB/B3LYP. Overall, the binding energy between a single atom of Pt and the substrate can increase by a factor of 2 via N-doping. This is due to the N atoms disrupting the delocalized double bond present in the substrate causing the C-Pt bond to use their 2s/6s orbitals more significantly. This is supported by molecular orbital and natural bond orbital data. In addition of this, the reduction in ΔG of H_2 and O_2 absorption on Pt, an indicator of its catalytic activity, was also reduced by a factor of 10 and 1.18 respectively. These effects were enhanced when occurring on the outside of the SWCNT and reduced on the inside of the SWCNT when compared to the graphene support.

[P1-40]

The Potential Energy Surface for hydrogen on Alkali-Graphite Intercalates: A Density Functional Theory Investigation

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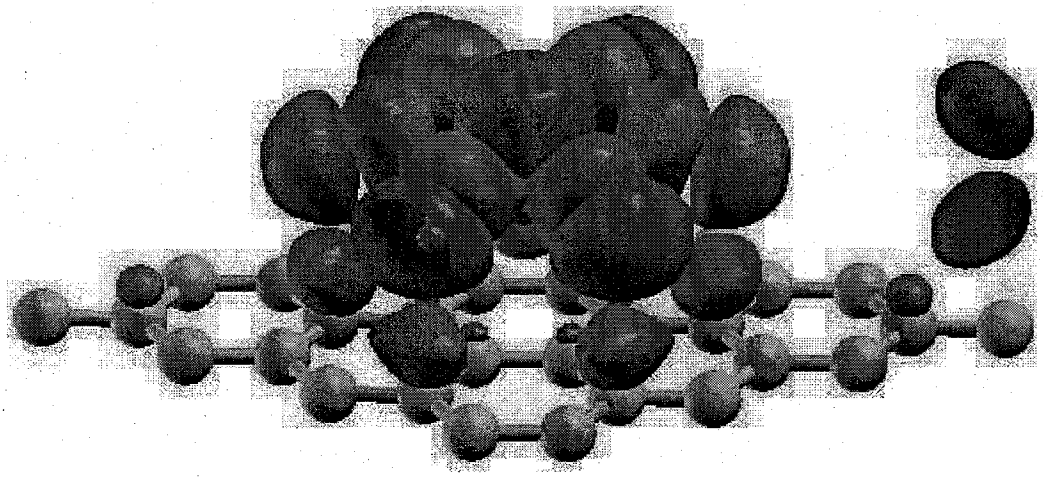
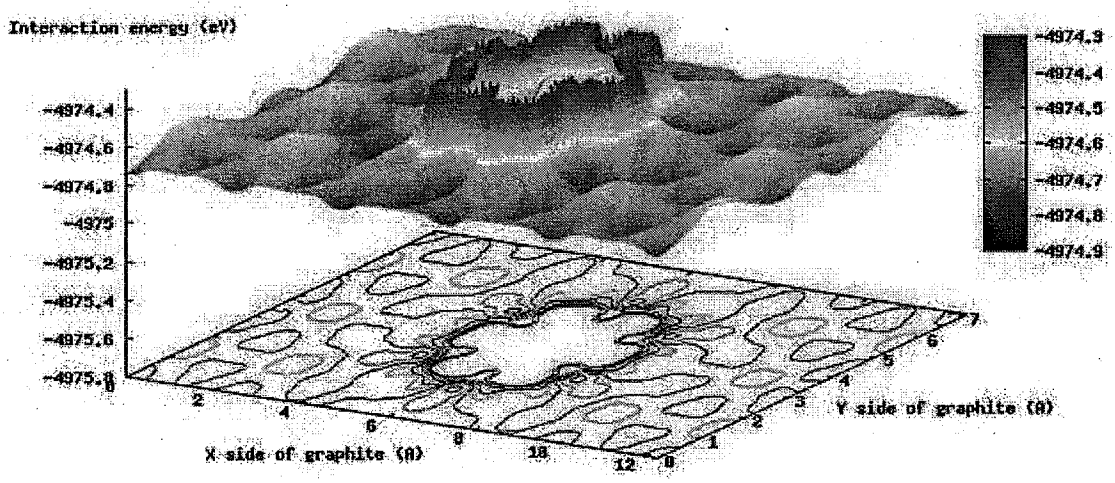
The potential energy surface for the system of hydrogen on alkali (Li, Na and K)-graphite intercalates surface have been investigated theoretically, where the structural, energetic, and electronic properties of the hydrogen on alkali/graphite system are studied through density functional theory (DFT) calculations using the gradient-corrected Perdew-Burke-Ernzerhof (PBE) approximation to the exchange-correlation energy. The calculations were performed using plane waves basis, and the electron-core interactions are described using pseudopotential. The wave functions and their energies for the hydrogen motion on the potential energy surface (PES) have been calculated and assigned by using discrete variable representation.

In first step of the studies, the global potential minimum corresponds to a scaned of hydrogen molecule on graphite surface, $R_{H...C}$=3.2A on *top* position, and the global minimun energy is -0.019041eV. The next step study are calculated the potential energy investigation of alkali atom on graphite surface and get same result that all metal stable on *hollow* position of graphite surface ($R_{Li...C}$=1.7A, $R_{Na...C}$=2.3A and $R_{K...C}$=2.6A) and a local minimum is also located, -1.37eV, -0.66eV and -0.96eV, for Li, Na and K, respectively. It can also be reported that a charge-density analysis shows that the origin of the increase in binding energy is the electronic charge transfer from the alkali atom to pi electron in the graphite.

The last step PES study investigation, the global potential minimum corresponds to a scaned of hydrogen molecule on alkali-graphite intercalates system are very anharmonic potential surface, ($R_{H...Li\text{-}graphite}$=2.6A, $R_{H...Na\text{-}graphite}$=2.7A and $R_{H...K\text{-}graphite}$=2.8) and a local minimum is also located, -0.081941eV, -0.078921eV and -0.070781eV, for Li, Na and K-graphite intercates system, respectively. It show that lithium doping give hydrogen higher capacity than another alkali doping. The results support and explain qualitatively the enhancement of the hydrogen storage capacity observed in some experiments of hydrogen adsorption on carbon compounds doped with alkali atoms.



Potential energy surface investigation of hydrogen-GICs system


Interaction energy (eV)
-4974.2
-4974.4
-4974.6
-4974.8
-4975
-4975.2
-4975.4
-4975.6
-4975.8
-4974.3
-4974.4
-4974.5
-4974.6
-4974.7
-4974.8
-4974.9
0
2
4
6
8
10
12
X side of graphite (A)
0
1
2
3
4
5
6
7
Y side of graphite (A)

[P1-41]

Computational Studies of $ZnR_2/ZnCl_2$ Reactions with Zincocenes and the Anomalous Formation of Decamethyldizincocene.

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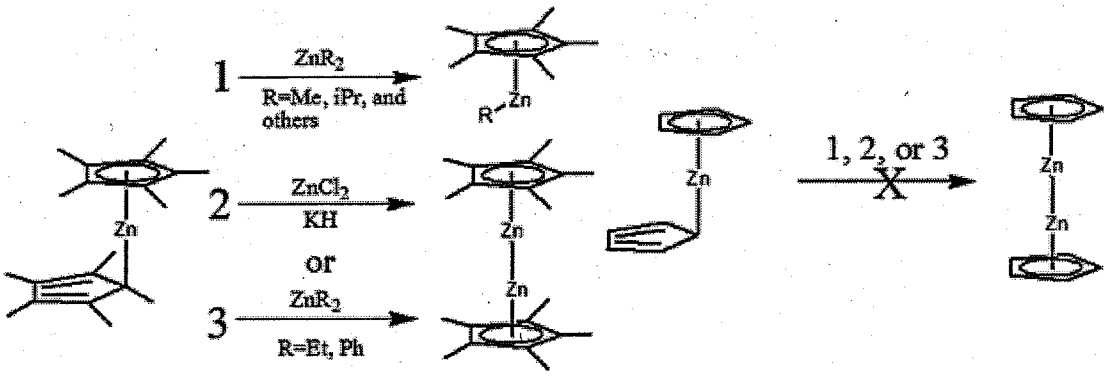
The unexpected discovery of decamethyldizincocene, $Zn_2(\eta^5\text{-}C_5(Me)_5)_2$, five years ago has given birth to an entirely new branch of organometallic chemistry: dimetallocene compounds featuring first-row transition metals. We have used Kohn-Sham density functional theory and Moller-Plesset 2nd-order perturbation theory to explore the formation of $Zn_2(\eta^5\text{-}C_5(Me)_5)_2$, via the reaction of decamethylzincocene, $Zn(\eta^5\text{-}C_5(Me)_5)(\eta^1\text{-}C_5(Me)_5)$, with ZnR_2 or $ZnCl_2$. It has been found experimentally that despite an array of choices for ZnR_2, only $ZnEt_2$ and $ZnPh_2$ react to form the target (dizinc) product, and these results will be analyzed theoretically. More importantly, theory will explain the reasons why the usage of the unsubstituted zincocene, $Zn(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)$, will not yield the dizinc product in any yield when reacted with $ZnCl_2$ or any ZnR_2.



[P1-42]

DFT study of the oxygen atom transfer reaction between DMSO and the molybdoenzyme DMSO reductase.

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The enzyme responsible for the dimethyl sulfoxide reduction is a mononuclear molydboenzyme, DMSO reductase (DMSOR). DMSOR serves as a terminal reductase in the bacterial respiratory chain where DMSO is used as an electron acceptor, catalyzing the overall reaction

$(CH_3)_2SO + 2H^+ + 2e^- \rightarrow (CH_3)_2S + H_2O$

In the present study we reinvestigate the oxygen atom transfer (OAT) reaction involving functional synthetic analogues such as $[Mo(OR)(S_2C_2H_2)_2]^-$ (R=Me, Ph). Our results provide a more direct comparison between previous theoretical and experimental findings.

The enzymatic mechanism of the OAT reaction is more complex than the reaction mechanism of any synthetic analogue, mainly due to the formation of an enzyme-substrate adduct prior to the appearance of the substrate-bound intermediate. This study also presents a possible mechanism for the formation of such adduct and subsequent OAT that involves a proton transfer to and from the substrate.

[P1-43]

Study of the Antioxidant Potential of Small Selenium-Containing Molecules

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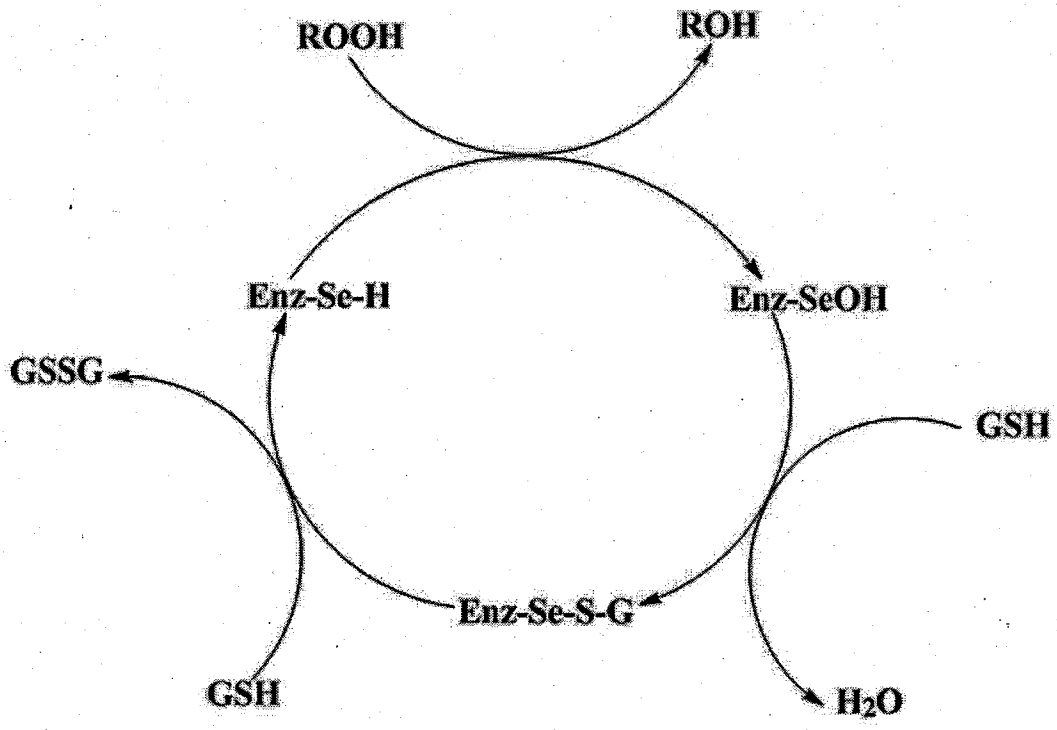
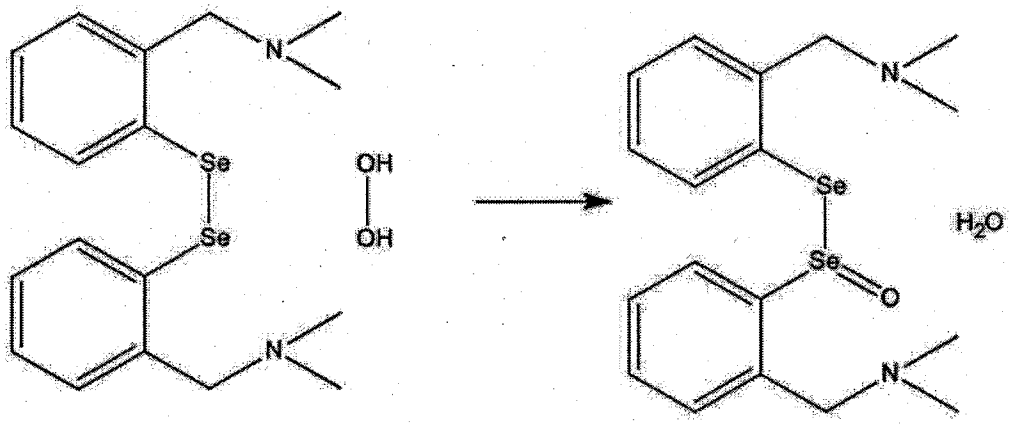
Selenoenzymes are known to reduce peroxides and other reactive oxygen species in the human body to protect tissue from oxidative damage. Research into selenoenzymes, such as Glutathione Peroxidase (GPx), has led to the development of small GPx mimic molecules that have similar reductive properties, making them potential drug candidates. Ebselen (2-phenyl-1,2-benzisoselenazol-3(2H)-one), and its diselenide and selenol forms, has been extensively studied because of its anti-inflammatory, antiatherosclerotic, and cytoprotective properties both in vivo and in vitro.



Density functional theory calculations at the B3LYP/6-311++G(3df,3pd)//B3LYP/6-31G(d,p) level have been performed to elucidate the mechanism and reaction energetics of the reduction of hydrogen peroxide by ebselen and its analogues, as well as tertiary amine analogues of ebselen diselenide and ebselen selenol. The effects of solvation are studied using the CPCM model or explicitly with water molecules added to the active site of the system. Various forms of the selenol are studied, including neutral, zwitterionic, and cationic with the amine protonated.



[P1-44]

Electron Correlation I: Theories

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Current methods for dealing with electron correlation include Moller-Plesset perturbation theory, configuration interaction, couple-cluster theory, and density functional theory. Recently, new concepts have been considered such as orbital functional theories[1,2], which may circumvent some of the drawbacks of conventional methods[3]. An overview of these theories will be presented. In an effort to develop a correlated energy expression, the CI problem has been expressed as an optimization problem using explicit energy expressions. Minimizing the explicit energy expressions through Newton-Raphson techniques provides insight into the form of a correlated energy expression, and also avoids matrix diagonalization.

[1] Goedecker, S.; Umrigar, C.J. *Phys. Rev. Lett.*, **1998**, *81*, 866-869.
[2] Nesbet, R.K. *Int. J. Quant. Chem.*, **2005**, *102*, 602-605.
[3] Staroverov *et al. Phys. Rev. A*, **2004**, *70*, 012502.

[P1-45]

Electron Correlation II: Properties

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For atoms and molecules, electron correlation energy has been shown to correlate well with the size of localized molecular orbitals.[1] More recently, ground-state atomic electron correlation energies, as well as their kinetic and potential energy components are shown to be well represented by empirical formulas which depend on the number of electrons, the atomic number and the electron density at the nucleus.[2] Here we investigate the electron correlation energy of atoms and small molecules as a function of a number of different properties. The properties include, the nuclear charge, the kinetic, Coulomb and electron-nuclear potential energies and the average interelectronic distance.[3,4]

[1] M.R. Peterson, R.A. Poirier, R. Daudel and I.G. Csizmadia, *Int. J. Quant. Chem.*, 19, 25 (1981).
[2] S. Liu and R. G. Parr, *J. Phys. Chem. A*, 111, 10422 (2007).
[3] J. W. Hollett and R. A. Poirier, *J. of Theoretical and Computational Chemistry*, 6(1), 13-22 (2007).
[4] J.W. Hollett and R.A. Poirier, Proceedings of *Modeling and Design of Molecular Materials 2008*, *Journal of Molecular Modeling*, 15, 739-745 (2009).

[P1-46]

The redox glycoside hydrolysis mechanism catalyzed by GlvA: A DFT Study

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The glycosidic bond of carbohydrates is one of the most stable biopolymeric bonds. In cells and organisms, glycosidic bonds are hydrolyzed by enzymes of the super-family glycoside hydrolyases. In particular, *B. subtilis* 6-phospho-α-glucosidase (GlvA) can hydrolyse both phosphorylated α- and β-D-glycosides and unphosphorylated α-D-glycosides. However, rather than directly attack the glycosidic bond, it has been proposed that the enzyme uses a hydroxylated metal ion (Mn^{2+}·····OH^-) and a coenzyme (NAD^+) to abstract a proton and hydride respectively, from the substrate. This introduces a double bond into the hexose ring. Ultimately, by shifting this double bond within the ring, the enzyme is thought to enhance the susceptibility of the glycosidic bond to cleavage. We have applied density functional theory methods to investigate the proposed mechanism of GlvA.

[P1-47]

Using a through-space modeling of substituent effects to study the dissociation of moderately strong acids in water by means of first-principles molecular dynamics simulations

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First principle investigations of the mechanism of acid dissociation and ion recombination in water are limited by the slow timescales that are usually involved in one of these processes, and by the fact that the bond-breaking/bond-forming events are actually driven by collective fluctuations of the solvent, the molecular details of which are poorly understood. Herein, we demonstrate that reliable insights into the molecular mechanism of acid dissociation can be obtained by employing unbiased molecular dynamics simulations in conjunction with a novel quantum mechanical/molecular mechanical (QM/MM) technique. The idea relies on a simple, yet accurate dipole-field approach for modeling the inductive effect of a chemical substituent on the Brønsted acidity of organic molecules, and on artificially "tuning" the value of the inductive effect to maximize the rates of the dissociation and recombination reactions. The strategy is exemplified in the case of monocarboxylic acids: First, by using gas-phase proton affinity, liquid-phase pKa, and dipole moment calculations, we demonstrate that a reliable QM/MM description of the acetic CH3COOH and of the trifluoroacetic CF_3COOH acids can be achieved by "cutting" the carbon-carbon bonds, provided that one employs hydrogen-capping (i.e.: H-COOH) in conjunction with an explicit point dipole representation of the electrostatic properties of the methyl and of the trifluoromethyl groups. Second, by adjusting the magnitude of the appropriately located point dipole moment, the aqueous acidity of the formic acid is increased until several dissociation/recombination cycles can be observed in a 100 ps molecular dynamics simulation. Analysis of the dynamical trajectories indicate that an important proton exchange channel consists of non-diffusive, ultrafast proton translocations over as much as 8 Å, in agreement with the recent interpretation of the pump-probe dissociation kinetics of photoacids that was put forward by Siwick and Bakker [Siwick, B. et al. J. Am. Chem. Soc. 2007, 129, 13412-13420].

[P1-48]

Calculation of arabinanase-ligand binding free energy by computer simulation: the challenge of oligofuranosides

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Furanosides are highly flexible compared to their pyranoside counterpart. This flexibility is considered to play in important role in the survival and pathogenicity of the organisms that produce them. Some of these organisms are responsible for infections such as Tuberculosis and C. difficile. Therefore development of novel vaccines and antibiotics for the prevention and treatment of the diseases are very important. In this study, solution simulations of an arabinanase protein and furanosides (protein-carbohydrate complex) were carried out to predict and understand their binding. Binding constants are calculated based on a directionally restricted potential of mean force (PMF) calculation. This technique can in principle predict very accurate binding free energy. The PMF was calculated by using umbrella sampling simulations. The system is simulated both in gas phase and in solution to observe the effect of solvation on the system. From the PMF equilibrium constants were calculated for the system. Conformational study of the furanosides was also carried out with classical, path integral and ab initio molecular dynamics simulations. 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.

[P1-49]

Effect of cholesterol on transport across membranes: a computational investigation

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Cholesterol is an integral component of cell membrane in human cells. Despite its importance, the mechanism by which cholesterol affects the passage of molecules into and out of cells remains a mystery. The primary objective of the present work is to investigate the role of cholesterol in the permeation process at the molecular level. Molecular dynamics simulations are carried out for hydrophilic as well as hydrophobic solutes inside model membranes with varying concentrations of cholesterol. Free energy profiles, which describe the thermodynamic contributions to the permeation process, are computed using the umbrella sampling technique. The effect of kinetics is also accessible from simulations through the diffusion coefficient. The effect of cholesterol is analysed in terms of the individual contributing factors and discussed based on the hydrophobic and hydrophilic nature of solutes.

[P1-50]

Molecular Dynamics Simulations of Sodium Dodecyl Sulfate Micelles Using a Coarse-Grained Model

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Surfactants are in general, relatively simple amphiphilic molecules, containing both hydrophobic (tail) and hydrophilic (head) groups. Therefore, they are soluble in both organic solvents and water. The insolubility of the hydrophobic fatty acid chains in an aqueous medium is balanced by a hydrophilic head group and determines the ability of the surfactants to form aggregated structures (micelles). Micelles are spherical lipid aggregates in which the hydrophobic tails are at the core and the polar head groups lie on the surface.

Molecular Dynamics Simulations have been widely used for investigation of surfactant self-assembly and micellar systems [1] which are possible mimetic for biological membranes. In practice, cellular processes cover time scales of nanoseconds to seconds and involve hundreds of different molecules interacting on a multitude of length scales. However, atomistic simulations have limited length and time scales.

In order to simulate large biological systems, simplification of the model is required. The idea of "coarse-graining" is to simplify the description of biomolecules through the "integration" of a large number of degrees of freedom into a few. The coarse-grained (CG) models are attractive alternatives to atomistic models, allowing simulations to be run on larger systems and longer time scales and still providing some realistic structural details.

In this work, a sodium dodecyl sulfate (SDS) micelle with 60 SDS molecules were simulated using the MARTINI coarse-grained force field. MARTINI force field, developed by Marrink et al [2], uses a four-to-one mapping to represent the molecules. It contains four main types of interacting centers: polar, apolar, nonpolar, and charged. There are also a number of subtypes which allow them fine-tuning of the interactions for special sites. The interaction of these particles are described by the Lennard-Jones and Coulombic potentials. Bonded interactions between chemically connected sites are described by harmonic stretching and bending potentials.

Each SDS molecule was represented by a 4-site model, one for polar headgroups and 3 four hydrocarbon tails. The micelle was prepared by putting SDS molecules over the surface of a C60 molecule as described by MacKerell [3]. This system was placed in a 65.3 Å cubic box and filled by 7579 water molecules. 10% of water molecules were replaced with anti-freeze water molecules described by Marrink [2]. 60 Na+ ions were added to neutralize the system. After the energy minimization, NpT simulations were performed for 520 ns at 300 K and 1 atm. A second simulation starting from a random initial configuration was also performed for 1 μs to study the self-assembly of coarse-grained SDS molecules.

In our simulations, the surfactants are aggregated in the form of a micelle with 59 SDS molecules. Several properties such as micelle size, shape, surface area, and torsional motion of hydrocarbon tails were calculated and compared with the results of all-atom simulations and available experimental data.

References:

[1] J.C. Shelley, M.Y. Shelley, Curr. Opin. Colloid Interface Sci., 2000, 5, 101.
[2] S.J. Marrink, A.H. de Vries, A.E. Mark, J. Phys. Chem. B, 2004, 108, 750.
[3] A.D. MacKerell Jr., J. Phys. Chem., 1995, 99, 1846.

[P1-51]

Estimate of acid constants for HCOO(aq) and OH(aq) using electron structure calculations

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Femtosecond pump-probe experiments on formate ions, $HCOO^-$, in aqueous solution show that one of the primary photoproducts following 200 nm photolysis is the formyloxyl radical, HCOO. The dynamics in the picosecond region suggests that HCOO(aq) is an acid. As its acid constant is unknown, we tried to estimate it using electron structure calculations. A number of aqueous clusters of the acid, [HCOO, nH2O] and its corresponding base, [$CO2^-$, H3O+, (n-1) H2O] were geometry optimized and the free energies were calculated. The difference in free energy between the acid- and base clusters with lowest free energy was assumed to approximate the standard state free energy change for the protolysis reaction. The calculations were performed for n = 10 and 14 with DFT using the basis sets 6-31G(d), 6-311+G(d,p), and aug-cc-pvdz. The calculations indicate that HCOO(aq) is a strong acid. Benchmark calculations on OH(aq) show reasonable agreement with thermodynamics.

Poster Session II (Thursday, July 23)

Arranged in alphabetical order

[P2-1]

Quantum Effects in Theoretical Investigations of Water Photolysis: $(H_2O)_2^+$ as a Case Study

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The photolysis of chemical compounds is an important reaction in astrochemistry, atmospheric chemistry, biological chemistry and nuclear chemistry. Although water is one of the most abundant compounds on earth and in the atmosphere, the possible photolysis mechanisms are still not well understood. Numerous molecular beam experiments on the photolysis of $(H_2O)_n$ clusters have demonstrated the presence of a H_3O species in the $(H_2O)_n^+$ cluster cations formed following photoexcitation. Many mechanisms have been proposed to explain the presence of the H3O fragment, and numerous computational investigations have been performed to elucidate the possible photodissociation reactions. To date, theoretical investigations have focused on the ionized dimer model, but they have relied on a classical description of the dynamics, and quantum effects have been largely ignored. In this work, we employ first-principles path integral-simulations to investigate the structure of the ionized dimer and the possible importance of quantum effects. In particular, the classical and centroid potentials of mean force are calculated for proton transfer in $(H_2O)_2^+$ and the proton transfer rates are determined according to transition state theory. The resulting classical and quantum mechanical pictures are compared in order to assess the importance of quantum effects.

[P2-2]

A Quantum-Mechanical Description of the Lennard-Jones Potential between QM/MM Subsystems

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QM/MM calculations currently neglect the effect of changes in the quantum subsystem's electronic structure on the non-bonded terms. A more physical model would allow variation of the Lennard-Jones (LJ) parameters during a simulation to reflect the changing QM environment, particularly important when the QM subsystem undergoes a chemical reaction. We propose a method, based on the exchange-hole dipole moment dispersion model of Becke and Johnson, to compute LJ parameters throughout QM/MM simulations for interactions across the subsystem boundaries. For a test case of the aqueous-phase S_N2 reaction of methylchloride and hydroxide, we show that there are large variations in the calculated LJ parameters along the reaction coordinate. This has a small, but significant, effect on the calculated free-energy surface. Accounting for dynamical changes in the quantum subsystem's electronic structure should be considered in ongoing QM/MM method development.

[P2-3]

Application of dispersion-corrected density functional theory to benchmark sets of intermolecular interactions

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The extension of density functional theory to account for van der Waals (dispersion) interactions is a longstanding problem and topic of active research, due to the importance of van der Waals forces in biomolecules and intermolecular interactions, and the failure of conventional GGA and hybrid functionals to describe dispersion interactions. We have previously shown that the Becke-Johnson dispersion model can be combined with standard GGA functionals (PW86 for exchange and PBE for correlation) to yield excellent binding energy curves for rare-gas diatomics [*J. Chem. Theory Comput.* **5** (4), 719–727 (2009)]. Here we present the application of the GGA+dispersion method to extended benchmark sets for intermolecular interactions, including hydrogen bonding, electrostatic interactions, small van der Waals complexes and biomolecular systems.

[P2-4]

Computational Study of Proper and Improper Hydrogen Bonding in Binary Methanol Complexes

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The importance of C-H...Y hydrogen bonding is well established in biochemistry, supramolecular chemistry, and crystal engineering despite the initial controversy over the previous decade. Our present study investigates the significance of the improper hydrogen bonding involving the methyl group in the binary complexes of CH_3OH with CH_3OH, H_2O, CH_3CN, CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. The stabilization energies, changes in geometry parameters, changes in harmonic frequencies and vibrational intensities upon complex formation were calculated at MP2/6-311++G (d,p) level of theory. The theory of Atoms In Molecules (AIM) was employed in the analysis of the electron density and the critical points properties, while the natural bond orbital analysis (NBO) was carried out to evaluate the orbital interactions within the pairs of the interacting atoms. Very good correlation is found between the stabilization energies, HB distance, and the topological properties of the electron density and the Laplacian of electron density. Calculated shifts in the frequencies of OH and CH stretching vibrations, changes in the vibrational intensities and the changes in the bond lengths are consistent amongst the systems investigated, as well as with the literature and the experimental observations. Further study is ongoing to gain better understanding of the nature of improper HB, as well as to explain the origin of the CH bond contraction in the blue shifted hydrogen bonds

[P2-5]

Exploring proton transfer pathways in the ammonia channel AmtB

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Most living organisms catalyze the transmembrane permeation of ammonium (in the form of either NH_3 or NH_4^+) by expressing proteins of the Amt/MEP/Rh family. Those proteins are key elements of the nitrogen regulatory system and are thought to facilitate nitrogen uptake in plants, yeast, and bacteria, and to help ammonium detoxification in mammals.

An important unresolved issue regarding the physiological role of these proteins is whether ammonium permeation is electroneutral (NH_3 permeation) or coupled to a net proton transfer (NH_3/H^+ co-transport). Although experiments are suggesting a net transport of either NH_3 or NH_4^+, depending on the organism studied [1], no proton transfer pathway has been found so far.

Using a combination of conventional (MM), polarizable (PM/MM), and quantum (QM/MM) molecular dynamics simulations, we examine the multiple binding modes of an ammonium (NH_4^+) substrate along the permeation pathway of Escherichia coli's AmtB protein, along with its propensity for transfering a proton to the protein or to the solvent molecules [2]. The QM/MM calculations are performed using the CP2K software [3].

[1] U. Ludewig, Ion transport versus gas conduction: function of AMT/Rh-type proteins, *Transfus. Clin. Biol.* **13**, 111-116 (2006).
[2] G. Lamoureux, M. L. Klein, and S. Bernèche, A Stable Water Chain in the Hydrophobic Pore of the AmtB Ammonium Transporter, *Biophys. J.* **92**, L82-L84 (2007).
[3] T. Laino, F. Mohamed, A. Laio, M. Parrinello, An efficient real space multigrid QM/MM electrostatic coupling, *J. Chem. Theory Comp.* **1**, 1176-1184 (2005).

[P2-6]

The Mechanism of Double Proton Transfer in Dimers of Uracil and 2-Thiouracil: The Reaction Force Perspective

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The intermolecular double proton transfer in dimers of uracil and 2-thiouracil is studied through density functional theory calculations. The reaction force framework provides the basis for characterizing the mechanism that in all cases has been associated to a dynamic balance between polarization and charge transfer effects. It has been found that the barriers for proton transfer depend upon the nature of the acceptor atoms and its position within the seminal monomer. Actually, the change in the nature of the hydrogen bonds connecting the two monomers along the reaction coordinate may favour or disfavour the double-proton transfers.

[P2-7]

Frozen Natural Orbitals for Ionized States within Equation-Of-Motion Coupled-Cluster Formalism

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The frozen natural orbital (FNO) approach, which has been used in ground state coupled-cluster calculations, is extended to open-shell ionized electronic states within equation-of-motion coupled-cluster (EOM-IP-CC) formalism. FNOs enable truncation of the virtual orbital space significantly reducing the computational cost with a negligible decline in accuracy. Implementation of MP2-based FNO truncation scheme within EOM-IP-CC is presented and benchmarked using ionized states of water, water dimer, nitrogen, and uracil dimer. The results show that the natural occupation threshold (i.e., percentage of the total natural occupation recovered in the truncated virtual orbital space) provides a more robust truncation criterion as compared to the percentage of virtual orbitals retained. Employing 99% - 99.5% of the natural occupation threshold, which results in the virtual space reduction by 70% - 30% in correlated calculations, yields errors below 1 kcal/mol. Moreover, the ionization energies (IEs) computed by EOM-IP-CC with singles and doubles (EOM-IP-CCSD) exhibit linear dependence as a function of the percentage of the natural occupation retained allowing extrapolation to the full virtual space values. The capabilities of the new method are demonstrated by calculation of the twelve lowest vertical IEs and the lowest adiabatic IE of guanine.

In addition to IE calculations, we present the scans of potential energy surfaces (PESs) for ionized water dimer. The scans demonstrate that the FNO truncation does not introduce significant non-parallelity errors and accurately describes PESs shapes and the corresponding dissociation energies.

[P2-8]

Oxidative Dealkylation Mechanism by Fe(II)-Dependent AlkB Family of Enzymes: A DFT Study

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Oxidative dealkylation is a unique mechanistic pathway found in the α-ketoglutarate-Fe(II)-dependent AlkB family of enzymes to remove the alkylation damage to DNA bases and regenerate nucleobases to their native state. The B3LYP density functional combined with a self-consistent reaction field was used to explore the triplet, quintet and septet spin-state potential energy surfaces of the multistep catalytic mechanism of AlkB. The mechanism was found to consist of four stages. First, binding of dioxygen to iron in the active-site complex occurs concerted with electron transfer, thereby yielding a ferric-superoxido species. Second, competing initiation for the activation of oxygen to generate the high-valent iron-oxygen intermediates (ferryl-oxo Fe^{IV}=O and ferric-oxyl Fe^{III}-O species) was found to occur on the quintet and septet surfaces. Then, conformational reorientation of the activated iron-oxygen ligand was found to be nearly thermoneutral with a barrier of ca 12 kcal/mol. The final stage is the oxidative dealkylation of the damaged nucleobase with the rate-controlling step being the abstraction of a hydrogen atom from the damaging methyl group by the ferryl-oxo ligand. For this step, the calculated barrier of 21 kcal/mol is in good agreement with the experimental activation energy of ca 20 kcal/mol for the enzyme-catalyzed reaction.

Liu, H.; Llano, J.; Gauld, J. W. *J. Phys. Chem. B* **2009**, *113*, 4887.

[P2-9]

TDDFT molecular dynamics simulations of the fragmentation of ionized biomolecules in gas phase and water environment

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Theoretical simulations are particularly well suited to investigate, at molecular level, direct and indirect effects of ionizing radiations in DNA, as in the particular case of irradiation by heavy ions. In the present work, we have studied the early stages of the fragmentation process of several ionized biomolecules in gas and liquid phase.

Fragmentation of water clusters containing 3 and 11 molecules with a total charge 2+ have been investigated in gas phase with Car Parrinello Molecular Dynamics [1] and Time-Dependent Density Functional Theory Molecular Dynamics simulations (TDDFT MD) [2]. Ionized species have been generated by removing two electrons from one of the four localized molecular Wannier orbitals of a target water molecule located in different positions. The charge evolution of the fragments has been analyzed by means of a grid-based Bader analysis [3], leading to fragmentation patterns in good agreement with results obtained in collision experiments with heavy ions [4].

The early stages of the Coulomb explosion of a doubly charged uracil molecule in both liquid and gas phase have been also investigated. Following the removal of two electrons from its deepest Kohn-Sham molecular orbitals, TDDFT MD simulations show that the doubly charged molecule explodes into four atomic fragments in less than 30 fs in gas phase, in very good agreement with the experimental observations [5]. When uracil is embedded in water, fragmentation leads exclusively to single atomic species: oxygen. We were also able to measure the indirect effects produced by direct ionization of a target water molecule near the uracil molecule. In this case the time propagation leads to the formation of a negatively charged oxygen atom within a few tens of femtoseconds.

References:
[1] M.-P. Gaigeot et al, J. Phys. B: At. Mol. Opt. Phys. **40**:1 (2007).
[2] I. Tavenelli et al, ChemPhysChem **9**:2099 (2008).
[3] W. Tang et al, J. Phys.: Condens. Matter **21**, 084204 (2009)
[4] L. Adoui et al, J. Phys B (2009) in press
[5] A. Le Padellec et al, Journal of Physics: Conference Series **101**, 012007 (2008).

[P2-10]

Threshold determination in the dissociation of $H_2(v,j) + H_2(v',j')$

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State-specific dissociation rate coefficients have been calculated for $H_2(v,j) + H_2(v',j')$ where E(v,j) and E((v',j') are less than 1 eV. The quasiclassical trajectory method was used on a chemically accurate potential for $H_2 + H_2$ [1]. At least 80000 trajectories were calculated at each energy on a grid of 0.054 eV from the energetic threshold for dissociation to 5 eV above the threshold. Larger batches were used in the threshold region to characterize the energy dependence.

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. However the probability of dissociation near the threshold is too low to be calculated efficiently with the quasiclassical trajectory approach while quantum calculations are intractable. Therefore it is necessary to estimate the excitation function near threshold in order to calculate the rate coefficient. 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, S. Raynor, and H. Teitelbaum, *Chem. Phys.* **50**, 175 (1980).

3. M. E. Mandy and P. G. Martin *Astrophys. J. Supp.* **86**, 199 (1993).

[P2-11]

Modeling cytotoxic activity of colchicine derivatives in different cancer cell lines

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Many cellular activities are dependent on the dynamics of microtubule polymerization and depolymerization. Small molecules like paclitaxel, vinca alkaloids, and colchicine are known to affect microtubule dynamics within the cell by binding to tubulin. However, these molecules bind to tubulin indiscriminately, leading to the death of both cancerous and healthy cells.

In this study, the focus is on the derivatives of colchicine which were tested against different types of cancer cells. Prediction models for predicting the cytotoxic activity of structural derivatives of colchicine in different cancer cell lines were developed based on computed molecular properties as descriptors. The prediction model is aimed at providing a tool for designing new and better colchicine derivatives that can differentiate between different cancer cell types.

[P2-12]

Silicon-29 Shielding Constants and Tensors Via Computational Methods

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Experimental silicon-29 nuclear magnetic resonance (NMR) is very cryptic. Due to the relatively small natural abundance of the ^{29}Si isotope (4.7%) no coupling is visible and every shift appears as a singlet. There are also many different possible structures in any given system, silicates as an example [1], which makes peak assignment almost a guessing game. Current computational techniques provide some relief to the problem of assignment, but methods do not reproduce experiment results consistently. We are developing a method capable of reproducing chemical shifts for a wide variety of tetra-, penta-, and hexacoordinate silicon compounds.

The ^{29}Si chemical shifts were calculated using hybrid density-functional developed by Perdew, Burke, and Enzerhof(PBE0), Dunning's correlation consistent basis sets (cc-pVnZ; n=D, T, Q), and the gauge including atomic orbital (GIAO) method as implemented in the Gaussian suite of programs. Input structures are taken from the crystal structures deposited with the Cambridge Crystallographic Data Centre. Crystallographic coordinates are converted into Cartesian coordinates for use in calculations using the Open Babel program. The extrapolated chemical shifts and corresponding tensors will be compared to experimental values and the most prudent method is presented.

[1] C. T. G. Knight, R. J. Balec, S. D. Kinrade, *Angew. Chem. Int. Ed.*, 2007, **46**, 8148.

[P2-13]

Five-Coordinate Silicon Complexes with Threitol and Erythritol

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The coordinating of open chain polyols to silicon in aqueous silicate solutions, forming hyper-coordinate bis-complexes, has been groundbreaking in the area of silicon biochemistry.[1] It has been suggested that the polyol needs to possess at least four adjacent hydroxyl groups with an internal pair in a threo-configuration.[2] By use of DFT calculations at the B3LYP/6-31++G(d,p) level of theory, optimized structures and relative energies were obtained for the penta-coordinate silicates of erythritol and threitol in all possible binding conformations, including internal and terminal binding site locations, in order to test the threo configuration characteristic. The obtained minima were treated in a Maxwell-Boltzmann distribution to obtain the percent composition of the penta-coordinate silicate complexes. The formation of the mono-bidentate complex is thermodynamically favourable, but the addition of a second polyol ligand makes for an even more stable complex. The bis-threitol silicates resulted in two most stable constitutional isomers, while the bis¬-erythritol resulted in three most stable constitutional isomers. The most stable bis-erythritol was found to be 0.31 kcal/mol more stable than the most stable bis¬-threitol. Using our recently developed method for assessing silicon-29 shielding constants, we have prepared sample nuclear magnetic resonance spectra based on the Boltzmann weights of the various constitutional isomers. Results are compared to experiment. Additionally, to characterize the hydrogen bonding stabilizing interactions within these systems, the topology of the electron density has been analyzed.

1. S. D. Kinrade, J. W. Del Nin, A. S. Schach, T. A. Sloan, K. L. Wilson and C. T. G. Knight, *Science.*, 1999, 1542.

2. S. D. Kinrade, E. W. Deguns, A.-M. E. Gillson and C. T. G. Knight, *Dalton Trans.*, 2003, 3713.

[P2-14]

Highly accurate momentum space pair densities and two-electron properties for the excited states of two-electron systems.

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The electron pair density, Γ, gives the probability density of finding an electron pair. Three-dimensional projections of Γ such as the one-electron, extracule, and intracule densities are easier to visualize. The one-electron density is the probability density of the position of an electron. The extracule density is the probability density for the position an electron-pair's center-of-mass and thus yields information on the location of the centroid of an electron pair. The intracule density is the probability density of an interelectronic vector and thus yields information on the relative motion of an electron pair. The intracule and extracule projections retain a pair-like quality which the one-electron density lacks. Complementary densities, both one- and two-electron, can be defined in momentum space. Only a very few calculations of the momentum-space two-electron densities have been published so far.

We consider the ground 1^1S and excited 2^3S, 2^3P, and 2^1P states of He and Li^+ as well as the ground state of H^-. Accurate wave functions expanded in Gaussian geminals with energy errors less than 3.5 nanohartrees are constructed. These wave functions can be transformed in closed form to momentum space, and the one- and two-electron densities and their projections can be obtained in closed form in both position and momentum space. A graphical analysis of these densities and related quantities is presented.

[P2-15]

Modeling the Ionization of Threonine in the Gas Phase

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A computational study of the formation of gaseous radical-cationic amino acid threonine, Thr•+, is important for the determination of ionization energy (IE) and for mass-spectrometric structural analysis. The experimental IE of Thr is not available in literature. This computational study finds that the IE could not be determined due to the facile fragmentation of Thr•+ upon formation either via ionization of its neutral conformer or from the Cu(II) complex. The latter is a soft technique used to produce Thr•+, which involves electron transfer dissociation, ETD, of the [(ligand) Cu(II)(Thr)] complex. Three proposed mechanisms of fragmentation of the complex are investigated using the B3LYP/6-31+G(d) level of theory with Gaussian03. The first mechanism involves the bond cleavage of Cu(II)-Thr resulting in the ETD of the complex and formation of Thr•+ and [(ligand) Cu(I)]; second mechanism is the loss of a neutral fragment from Thr to form [(ligand) Cu(II)(Thr-b)]; third mechanism is the simultaneous ETD of the complex and fragmentation of Thr. The zwitter-ion and molecular forms of the [(ligand) Cu(II)(Thr)] complex as well as possible rearrangements of these isomers were investigated. Preliminary results of the molecular isomer illustrate that the second proposed mechanism for the molecular [(ligand) Cu(II)(Thr)] complex is likely to be occurring.

[P2-16]

Solapsone as a Disease Modifying Drug for Alzheimer's Disease

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Alzheimer's disease (AD) is the most common neurodegenerative disorder, affecting more than 25% of the elderly population in developed countries. Although there are treatments available for the management of AD (e.g. donepezil), these are symptomatic agents that have no effect upon the natural history and course of the disease. Accordingly, there is an urgent need for the design and discovery of new drugs for the curative management of AD. To achieve this goal, we are using in silico design methods to identify compounds capable of binding to beta-amyloid peptide, thereby precluding its neurotoxic aggregation. To ensure the identification of drug-like compounds we have searched libraries of known drug molecules to identify drugs being employed for other therapeutic indications for their ability to bind to beta-amyloid. From this process we identified solapsone, a compound used to treat leprosy in the 1940s and 1950s. Using the CHARMM22 force field in MOE, molecular modelling simulations were performed to explore the capacity of solapsone to bind to the HHQK and LVFF regions of beta-amyloid. Multiple starting conformations of beta-amyloid were obtained from the Protein Databank. Solapsone has demonstrated an energetically favourable capacity for binding to these regions through hydrogen bonding, aromatic-aromatic and cationic-aromatic interactions. This binding occurs at multiple sites and thus indicates solapsone's potential to prevent beta-amyloid aggregation.

[P2-17]

Effects of 8-Aryl Substituents on the Structure and Stability of Purine Nucleic Acids

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Aryl radicals can react with DNA to afford C8-aryl deoxyguanosine (dG) adducts. In nature, this type of adduct can be generated due to the presence of carcinogenic arylhydrazines, polycyclic aromatic hydrocarbons, and phenolic toxins. These C-bonded DNA adducts can be accompanied by abasic site formation. In order to understand the effects of aryl substituents (with varying steric and electronic properties) on the rate of deglycosylation, DFT structural studies were performed on a family of nucleoside and nucleobase adducts, and the N7 proton affinities of the adducts were evaluated. Changes in the structure going from the nucleoside to the nucleobase provide a rationale for differences in the experimentally measured rates of hydrolysis. The relative effects of protonation, glycosidic-bond orientation, and the addition of the aryl group on the stability of the nucleoside can be compared through differences in the calculated deglycosylation barriers. The effects of larger nucleotide models on the preferred structures of the adducts was also considered to help understand the relevance of our findings to larger DNA systems.

[P2-18]

The Baeyer-Villiger Reaction: Ionic or Neutral?

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The Baeyer-Villiger (BV) reaction which involves the oxidation of a ketone to an ester or lactone, is a powerful and frequently employed synthetic tool. Even though this reaction with organic acids and peracids normally takes place in non-polar solvents, a variety of ionic mechanisms are reported in standard organic chemistry texts. In clear contradiction with this type of mechanism are the experiments of Hawthorne and Emmons (J. Am. Chem. Soc.1958, 80, 6398) that show an increase in the rate constant of several BV reactions when the polarity of the solvent is decreased. Our DFT calculations indicate that the least energetic reaction pathway in non-polar solvents is non-ionic and fully concerted (J. R. Alvarez-Idaboy, L. Reyes, N. Mora-Diez, Org. Biomol. Chem. 2007, 5, 3682). We then focus on the reaction of propanone with performic acid, in the presence of formic acid as catalyst, to study solvent effects on this mechanism. Furthermore, different possible reaction pathways, ionic and non-ionic, that could take place in water are compared to get a better picture of how solvent polarity affects the kinetics of this reaction. Our calculations indicate that the experimental findings of Hawthorne and Emmons should still apply in more polar solvent mixtures. The study that will be presented puts into question the general assumption that organic reaction mechanisms in solution always involve ions.

[P2-19]

Extending the Time-Scales Accessible in Molecular Dynamics Simulations of Reactions

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Molecular dynamics (MD) is a powerful tool for studying chemical systems. To properly model reactions with MD, it is necessary to calculate the atomic forces using quantum chemical (QC) methods. QC methods are computationally-intensive and limit the time-scales accessible in MD simulations to the sub-nanosecond regime, which is too short to observe most chemical reactions. To overcome this time scale limitation, while retaining the ability to describe reactions, we are exploring ways of combining QC methods with less demanding force-fields (FFs). Specifically, we are developing an MD technique in which the system is modeled predominantly with an FF, while monitoring its behaviour for the onset of potential reactive events. When a potential reactive event is detected a switch is made to QC methods, and when the reaction is complete, the system reverts to an FF description. Since reactive events occur very infrequently, and proceed quickly when they do occur, this method significantly reduces the use of QC methods in MD simulations, thus extending the time scales accessible in these simulations. Meanwhile, the use of QC methods during reactive events ensures changes in bonding are described properly. In this presentation, we will discuss the basic features of this methodology and demonstrate how it can be used to extend by orders of magnitude the time scales accessible in MD simulations of reactions. The limitations of this methodology will also be discussed.

[P2-20]

Quantum-classical dynamics in the mapping basis and its relation to the subsystem basis

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Quantum-classical dynamics is a promising method for simulating large many body systems. But its simulation presents a number of difficulties, mainly due to the fact that the quantum and classical subsystems are treated on different footings. In order to overcome this difficulty, we represent the quantum-classical Liouville equation in a mapping basis. An approximate solution of the resulting equation can be obtained by Newtonian dynamics in the full phase space of the system.
In this work, we establish the relation between the mapping and the subsystem bases.

[P2-21]

Do point mutations evoke disperse entropic changes throughout a protein domain?

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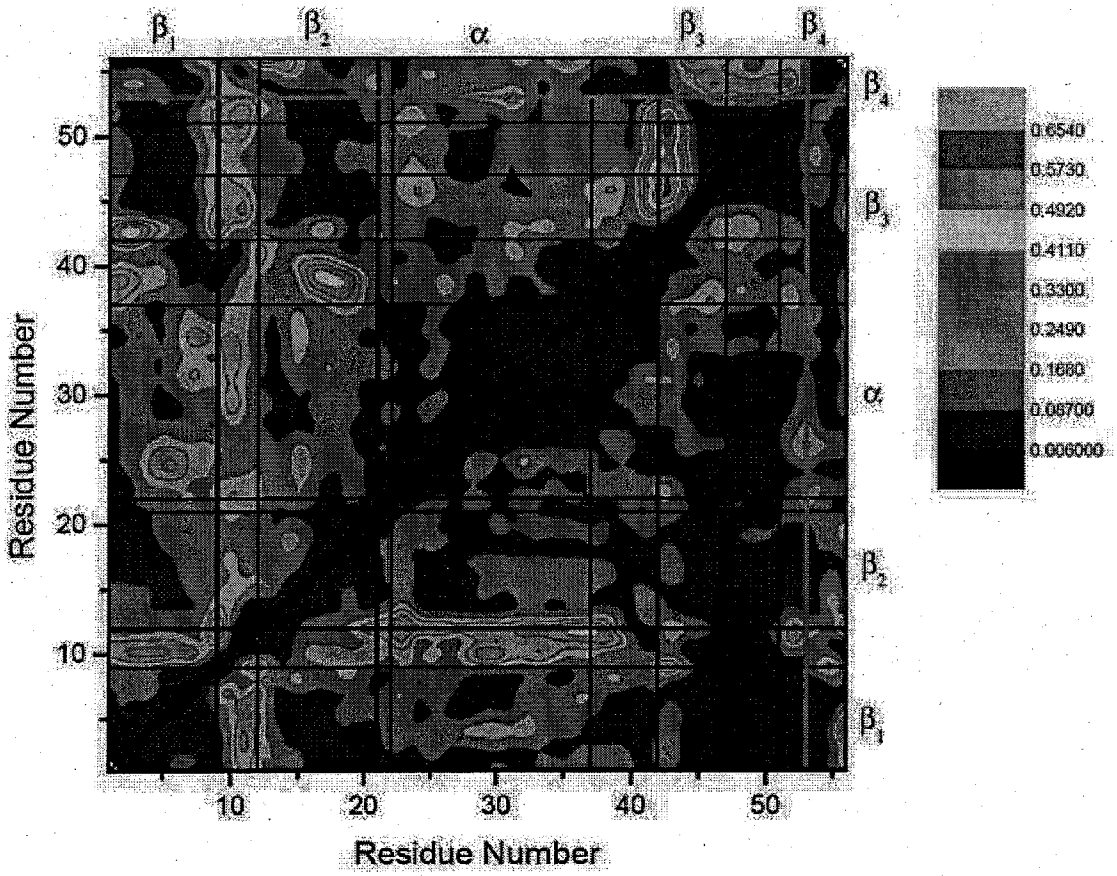
The 56 amino acid B1 domain of Protein G from Streptococcus exhibits thermal stability over a broad range of temperatures. It is known experimentally that the thermal stability of the protein changes, sometimes dramatically, when amino acid substitutions are introduced at position 53. Experimental attempts to attribute this to locally-induced perturbations, such as steric effects and solvent interactions, have failed. To explore and quantify the remaining possibility, that point mutations have significant non-local effects on protein structure, we performed molecular dynamics (MD) simulations on the wild type B1 domain and several of its mutants. We then re-sampled, with replacement, the mutant trajectories one thousand times, each time subjecting the resulting conformations to principal component analysis of their inter-C_α distances, followed by Procrustes-rotation of the factors to best fit those of the wild type. Our results suggest that the thermal stability of the mutants decreases as the fit of their Procrustes-rotated factors to the wild type B1 domain deteriorates. We will discuss how figures such as that illustrated below demonstrate that extreme deviations of fit are attributable to amino acid residues within secondary structure elements far-removed from the site of mutation.



Deviations from the from the wild type resulting from mutation at position 53 in B1 domain of Protein G. Plotted is the Procrustean-rotated principal components of the mutants deviation from the wild-type principal components of 1000 trajectories. Top panel: T53P (Tm

[P2-22]

The Performance of DFT in Prediction of Radical-Cationic Amino Acids

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The ionization of gaseous amino acids and peptides followed by collision-induced dissociation, CID, of radical-cationic products is widely used in mass-spectrometric structural determination. The CID technique implies kinetically-controlled fragmentations; thus, the tedious QM calculations of possible reaction profiles with all transition states located are used in MS in order to assign spectra. Despite the fact that DFT often drops the reaction barriers (kinetic stability) for radical cations, the hybrid B3LYP functional is by far the most widely used since the size of the systems is prohibitive for the post-HF methods. In our study we explore the reliability of several popular exchange-correlation functionals with 20% to 50% of exact exchange and the possible usage of the DFT failure. The ionization of 20 gaseous α-amino acids was examined using B3LYP, BHandHLYP, and M052X within QM approach and the GAUSSIAN03 program. The CPMD trajectory calculations based on the GGA BLYP exchange-correlation functional were performed for selected radical-cationic amino acids, which exhibit spontaneous or low-energy fragmentations upon ionization. The IEs predicted with hybrid functionals are in excellent accord with experimental values available. Hybrid DFT also unmistakably predicted thermodynamic/kinetic instability of 6 amino acids for which experimental IEs could not be determined due to facile fragmentations upon ionization. B3LYP drops considerably the reaction barriers to the Cα –C(side chain) cleavage for aromatic amino acids; the barrier becomes vanishingly small with BLYP. The benefit of this failure is that the BLYP-based CPMD simulations show very fast dynamics and, for the systems considered, unmistakably determined the lowest-energy fragmentation mechanisms.

[P2-23]

Can Correlation Bring Electrons Closer Together?

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The exact Coulomb hole for the ground state of the helium atom and helium-like ions is presented. We find that the correlated wavefunction yields a smaller probability of finding the electrons at large separations than does the Hartree-Fock wavefunction, implying that correlation brings distant electrons closer together. This effect becomes less pronounced as the nuclear charge increases.

[P2-24]

Modeling the Hydrolysis of DNA Nucleosides

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The deglycosylation of DNA nucleosides under neutral conditions has been studied for decades; however, few computational studies have been able to correctly predict the mechanism for hydrolysis of the N-glycosidic bond. The current study uses a hybrid solvation technique to generate a small model for the hydrolysis of 2'-deoxynucleosides. The model is initially generated using 2'-deoxyuridine as a test case, and is further assessed for both the purines (2'-deoxyadenosine and 2'-deoxyguanosine) and the remaining pyrimidines (thymidine and 2'-deoxycytidine). Through the use of two-dimensional reaction energy surfaces, it is found that the correct (stepwise) mechanism is only predicted if explicit water molecules and implicit (PCM) solvation is included during the optimization step, rather than as a correction to the gas-phase surface. The correct trend in Gibbs energies of activation are found for all nucleosides (except 2'-deoxyguanosine) and the barriers calculated compare well to the experimentally derived values. This study shows that while solvent-phase single-point energy corrections may yield experimentally acceptable values, care should be taken when making structural conclusions from gas-phase optimizations involving charge-separated transition states and intermediates.

[P2-25]

Approximation Level of Calculation Effects in the Estimation of Intermolecular Electronic Charge Transfer in Lewis Type Acid-Base Adducts

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Using computational chemistry as a tool, two Lewis type acid-base adducts: NH_3--BF_3 (A1) and NH_3--SO_3 (A2) have been examined. Such task was performed conducting several procedures at estimating the amount of charge (Mulliken, Chelp and AIM) transfer involved in their intermolecular interactions. The Density Functional Theory (DFT) method at different approximation levels for calculation was used along with the functional B3PW91 and a series of basis sets of correlation consistent cc-pVXZ (X = D, T, Q). In order to be able to obtain good matching between the intermolecular charge transfer calculations and experimental data to accomplish the estimation of such charge transfer, it was necessary for the A1 case, only to use a high level of approximation in DFT calculations whereas for the A2 case, was also necessary to use a high level of calculation in its geometry optimization. The Chelp method is the one that allowed obtaining more exact results.

[P2-26]

Refinement of a Continuum Electrostatics-Dispersion Model of Solvation. Prospective Studies and Retrospective Analyses from the SAMPL Challenges.

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Changes in hydration free energy upon complex formation are a ritical component of binding affinities in aqueous solution. Hence, simulation methods that aim to predict binding free energies require accurate solvation models to achieve their goal. Over the years, much effort has been expended in developing and parameterizing solvation models at various levels of theory. These invariably involve the use of published datasets of vacuum-to-water transfer free energies of small molecules that are divided into training and validation subsets. Experimental data are available for a few hundreds of small organic molecules. These molecules are quite similar, mostly monofunctional, with a sprinkling of still relatively simple polyfunctional molecules. In contrast most organic molecules of biological interest, e.g., drug molecules, are highly polyfunctional.

In the past two years, new test sets became available through the SAMPL blind prediction challenges sponsored by OpenEye Scientific Software. The structures of the molecules were made available to the public a few months before the experimental transfer free energies were disclosed, allowing a true test of prediction methods.

In SAMPL-1 (2008), the prospective dataset for transfer free energy predictions consisted of 63 drug-like, diverse, polyfunctional, neutral but polar compounds, with examples of transfer free energies and molecular weights larger than ever before seen in the common public datasets of neutral compounds.

The SAMPL-2 (2009) challenged the solvation models with additional 23 drug-like molecules including such relevant compounds for biomolecular systems like glucose, xylose, uracil, caffeine, aspirin and ibuprofen. SAMPL-2 also challenged predictors to explain the publicly available but unexpected transfer free energies for 8 compounds.

We participated in both SAMPL blind prediction challenges using a continuum model of hydration including continuum solute-solvent dispersion-repulsion contributions, a surface-area-based cavity contribution, and electrostatic contributions from a boundary element method.

In SAMPL-1 we tested prospectively a continuum electrostatics-dispersion model with parameters calibrated and tested against experimental data from the commonly available data sets.

For SAMPL-2, we developed and tested prospectively the First Shell Hydration (FiSH) continuum model, a reformulation of our previous continuum model against explicit water molecular dynamics simulation
and Linear Interaction Energy (LIE) data, aiming to capture the nature of the first water shell in continuum models.

[P2-27]

Theoretical studies on the structural change in the N-protonated Tetra(p-hydroxyphenyl)porphyrin

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Porphyrins in particular are well-known for their tendency to aggregate in acidic solution, resulting in perturbations to their electronic absorption spectra. In nature, assemblies of porphyrin derivatives are exploited by photosynthetic plants and organisms for their light-harvesting capabilities. The porphyrin TCPP is known to form aggregates in aqueous solution in acidic media due to its transition to the diacid form H_2TCPP. The diprotonated species H_2TCPP aggregates, depending on its concentration, pH, and ionic strength. On the basis of a study of the N-protonated Tetra(p-hydroxyphenyl)porphyrin (H_2TCPP) in the protonation process was calculated by using the B3LYP/3-21G method under certain symmetry restrictions.

[P2-28]

Polyglutamine Monomer Structure and its Implications for Molecular Self-Assembly

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Polyglutamine is a naturally occurring peptide found within several proteins in neuronal cells of the brain, and its aggregation has been implicated in several neurodegenerative diseases, including Huntington's disease (HD). The resulting aggregates have been demonstrated to possess beta-sheet structure, with the constituent beta-strands arranged perpendicular to the long axis of the fibril ("cross-beta" structure), and aggregation has been shown to start with a single misfolded peptide. We computationally examined the structural tendencies of three mutant polyglutamine peptides that were studied experimentally, and found to aggregate with varying efficiencies. Low-energy structures have been generated for each peptide by simulated annealing molecular dynamics in NAMD, and analyzed quantitatively by various geometry- and energy-based methods.

According to the results of this work, the observed inhibition of aggregation appears to be due to localized conformational restraint on the peptide backbone, which effectively confines the peptide backbone to native random coil structure, thereby discouraging transition towards the β-sheet structure required for aggregate nucleation/growth. Such knowledge will prove quite useful to the design of future aggregation-inhibiting treatments for Huntington's and other related diseases.

[P2-29]

Polarization and Permittivity of Nanocomposites through MD and DFT

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Using GaussView, a spherical 51 atom α-quartz (silica, SiO_2) crystal structure was bonded to the free epoxy-opened ends of a 116 atom chain built from 2 DiGlycidyl Ether of Bisphenol A (DGEBA) epoxy monomers and a 1,3-diaminobenzene hardening agent. The conformation of the flexible chain was then optimized with molecular mechanics in Gaussian using either UFF or the DREIDING force field with tight convergence criteria. Then with SIESTA, using the GGA and PBE functional and DZP basis set, static electric fields were applied in the three cartesian axes and the polarizability (α) matrix was calculated from both the change in energy and change in dipole moments. Plots of dipole moment with respect to the field revealed a strong linear dependence; the slope giving the respective matrix elements (α_{ij}). The mean polarizability was calculated to be 99.8 $DÅV^{-1}$ ($2.02x10^3$ a.u.). Energy plots with respect to the field gave poorer fits to a quadratic; the second derivative giving α, with a mean polarizability of 102 $DÅV^{-1}$ ($1.55x10^3$ a.u.).

Again in GaussView, three Poly(VinyliDene) Fluoride (PVDF) chains of 12 monomers each were chemisorbed onto the surface of a 13 atom silver cluster. The chains were wrapped about the inclusion by twisting dihedral angles; and the NPT ensemble was optimized and packed to the appropriate density in a periodic box using GROMACS v.4.0.2 with the G45a3 united-atom force field. The structure was then relaxed again with SIESTA, and polarization will be calculated using the built in feature.

Future work aims at calculating the dielectric tensor, (or similarly the electrical permittivity), the percolation limit, the effect of inclusion size and shape on dielectrical properties, as well as time dependent response to oscillating fields.

[P2-30]

Noncovalent Interactions at Natural or Damaged DNA Nucleobase-Protein Interfaces

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The interactions between DNA and proteins are vital for the survival of living organisms. For example, repair of DNA damage relies on nucleobase-amino acid interactions to identify and remove only damaged nucleobases. DNA alkylation, which is a common type of DNA damage and leads to cationic nucleobases, can be repaired by enzymes (DNA glycosylases) that selectively recognize and remove damaged bases. Unfortunately, however, the mechanism for this repair is not well understood. Clues about the mechanism have been obtained from recent crystal structures of DNA glycosylases, which indicate that modified nucleobases may be held in the active site by aromatic amino acid residues. The types of interactions used by proteins to recognize specific DNA/RNA bases have been proposed to be weak, noncovalent interactions. Although hydrogen-bonding interactions between biological systems have been extensively investigated, detailed studies of stacking and T-shaped interactions between DNA and protein fragments are not as well understood. Therefore, the present work uses highly accurate computer calculations to study these weak interactions between DNA and RNA nucleobases or damaged cationic nucleobases and the aromatic amino acids. Our calculations reveal the magnitude of these interactions, as well as the attractive nature of the bonding present between biological building blocks, which will further aid our understanding of the mechanism of action of these unique DNA repair enzymes.

[P2-31]

Effect of alkyl chain length on the interaction between phenolic esters and water molecules

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Polyhydroxyl phenols are known to be important in protein-binding and protective coatings. A series of novel phenol-based glycerolipids, including 1,2-dipalmitoylgalloylglycerol (DPGG), have been recently proposed which are expected to be useful for biocompatible coatings and biosensing applications.[1,2] Monolayers of DPGG show strong lateral cohesion, which can be related to hydrogen bonding between headgroups. In this regard, molecular dynamics (MD) calculations can provide valuable information concerning hydrogen bonding interactions in lipid monolayers. In this work, MD simulations are performed to investigate the effect of alkyl chain length on the interaction between several phenolic esters and water clusters of varying sizes. This procedure can be considered as a first stage in studying the characteristics of the novel phenol-based glycerolipids at the air-water interface.

1. R. Schmidt, J. G. Carrigan, C. E. DeWolf, Can. J. Chem. 84, 1411, 2006
2. R. Schmidt, C. E. DeWolf, Langmuir 20, 3284, 2004

[P2-32]

Detailed assignment of UV-vis absorption spectra of high spin heme derivatives

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Despite the large significance of high spin ferric heme in biology, detailed assignments of UV-vis absorption data of corresponding species are missing. Recently there have been reports of unexplained enhancement of some A1g Raman modes (particularly v4) in several metalloporphyrins including hemin, hematin, β-hematin, Fe(III) porphine chloride, Fe(III) tetraphenylporphine chloride, Fe(III) tetraphenylporphine μ-oxo dimer, and Fe(III) octaethylporphine chloride at near-IR excitation; however, interestingly this feature is not observed in Fe(III) octaethylporphine μ-oxo dimer, hematin μ-oxo dimer, and hemoglobin [1,2]. To gain more insight into the mechanism of Raman enhancement there is a need for detailed assignment of optical absorption bands of these compounds. In this study, extensive time-dependent density functional theory (TD-DFT) computations are carried out applying a high basis set (TZVP) [3] to calculate electronic transitions of heme derivatives.

The calculated results are found to be in reasonable agreement with the observed (and reported) UV-vis absorption and magnetic circular dichroism data. In correlation to resonance Raman results, this allows for a detailed assignment of the optical spectra of high spin ferric heme derivatives.

1. Bayden R. Wood, Steven J. Langford, Brian M. Cooke, Janelle Lim, Fiona K. Glenister, Martin Duriska, Jessica K. Unthank, and Don McNaughton, J. Am. Chem. Soc. 126, 9233, 2004

2. R. Puntharod, G. T. Webster, M. Asghari-Khiavi, K. R. Bambery, F. Safinejad, K. J. Haller, B. R. Wood, Submitted

3. A. Schaefer, C. Huber, R. Ahlrichs, J. Chem. Phys. 100, 5829, 1994

[P2-33]

Biomimetic water oxidation: some clues from computational chemistry

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The splitting of water by photosynthesis organisms is one of the most remarkable phenomena in nature, and the oxygen evolving centre (OEC), a tetra manganese cluster found in the Photosystem II, is central to this process [1]. However, detailed chemical steps involved in the oxygen evolution and precisely how such highly active species avoid oxidative damage to the surrounding protein environment remain a mystery. In developing our understanding of photosynthetic water oxidation, synthetic oxygen evolving complexes (small molecular mimics of the OEC) are critical. We use density functional theory (DFT) to explore biomimetic Mn-based oxygen evolving complexes synthesised by Naruta and co-workers [2] and McKenzie and co-workers [3]. DFT calculations on these systems suggested that 'metal-oxyl character' [Mn(IV)-$O^{\cdot+}$], as distinct from the metal-oxo form [Mn(V)=O], is the common denominator for the O-O bond formation. In cases where the oxyl radical character is 'masked' in the ground state by electron transfer from either the metal or the porphyrin co-ligand, the interaction between oxidant and substrate is repulsive at large separations, only becoming attractive when the incoming nucleophile approaches close enough to drive an electron out of oxide $p\pi$ manifold, thereby 'unmasking' the oxyl radical [4]. The active role of substrate in unmasking the oxyl radical character of the Mn(V)=O unit offers the potential for discrimination that is one of the defining features of the oxygen evolving centre, and may represent a general framework for understanding structure function relationships in water oxidation catalysts.

References:

[1] K. N. Ferreira, T. M. Iverson, K. Maghlaoui, J. Barber and S. Iwata, *Science*, 2004, 303, 1831.
[2] (a) Y. Shimazaki, N. Nagano, H. Takesue, B. H. Ye, F. Tani and Y. Naruta, *Angew. Chem.* 2004, 116, 100. (b) Y .Naruta, M. Sasayama and T. Sasaki, *Angew. Chem. Int. Ed. Engl.* 1994, 33, 1839.
[3] (a) A. K. Poulsen, A. Rompel and C. J. McKenzie, *Angew. Chem. Int. Ed.* 2005, 44, 6916. (b) C. Baffert, M. N. Collomb, A. Deronzier, S. K Knudsen, J. M. Latour, K. H. Lund, C. J. McKenzie, M. Mortensen, L. P. Nielsen and N. Thorup, *Dalton Trans.* 2003,1765.
[4] (a) W. M. C. Sameera and J. E. McGrady, *Dalton Trans.* 2008, 6141. (b) A. E. Anastasi, P. H. Walton, J. R. L. Smith, W. M. C. Sameera and J. E. McGrady, *Inorg. Chim. Acta* 2008, 361, 1079.

[P2-34]

Symmetry-broken independent-particle models in Born-Oppenheimer molecular dynamics of chemical bond dissociation

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Simulating chemical bond dissociation dynamics requires electronic structure methods to seamlessly describe the transition from the initial closed-shell configuration to an open-shell intermediate. Challenges in locating symmetry-broken potential energy surface are demonstrated on direct-dynamics simulations of the $RO\text{-}NO_2$ bond dissociation in nitric esters. The second derivative of the unrestricted energy with respect to nuclear displacement is shown to be discontinuous at the onset of symmetry breaking, in analogy with the discontinuous specific heat in the Landau theory of second-order phase transitions.

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[P2-35]

Testing the performance of DFT-D corrections for hydrocarbons: enthalpies of hydrocarbon isomerizations and olefin polymer growth reactions

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Recent progress in DFT theory and software allows for the modeling of systems like TM-catalyzed hydrocarbon transformation (polymerization, metathesis, etc.) with realistic models. However, it was found out that for the larger systems, commonly used black-box DFs might have errors. Particularly difficult is the treatment of inter- and intra-molecular dispersion interactions in hydrocarbons – the latter being popular ligands like Cp* or reactants/products (the polymer's growing chains). In this work we have applied the simple DFT-D approach by Grimme with common hybrid and GGA DFT methods for the modeling of the enthalpies of reactions of the growth of common polyolefins; we also review and reproduce some of the previously done benchmarks in the area: alkane branching and relative stability of isomers of $C_{12}H_{12}$ and $C_{10}H_{16}$. In addition, computations with correlated wavefunction methods (MP2) and the new functionals B97-D and M06-L were performed. Results show that (1) inclusion of DFT-D is essential for a proper description of the enthalpies of reactions of polymer growth and hydrocarbon branching; (2) even with the correction, not all DFs are accurate, however the best functionals BPBE-D and PBE-D give qualitatively correct results; (3) the B88 + LYP combinations of DFs fail for polycyclic hydrocarbons like octahedrane $C_{12}H_{12}$, and this problem is seemingly unrelated to the dispersion. The octahedrane is not the most stable $C_{12}H_{12}$hydrocarbon for all the methods predict dimethyl-naphtalines to be of lower energy. The performance of the special density functionals B97-D and M06-L is in general similar to the best DFT-D corrected GGA functionals (BPBE-D and PBE-D); however, B97-D has large errors for the stability of octahedrane $C_{12}H_{12}$.

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[P2-36]

Binuclear Uranium(VI) Complexes with a "Pacman" Expanded Porphyrin: a Computational Probe for Unusual Bis-Uranyl Structures

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Early *f*-elements like uranium possess interesting possibilities that arise from the accessibility of *s*, *p*, *d* and *f* orbitals to chemical bonding, thus allowing for exciting coordination chemistry. For uranium in the oxidation states of (V) and (VI), the most characteristic and stable form is the linear UO_2^{n+} moiety, the uranyl ion. Recently, Arnold et al. have shown that a pacman-like polypyrrolic ligand H_4L can accommodate one uranyl ion but the second N4-coordination site of the ligand remains metal-free, i.e. mononuclear $(UO_2)(H_2L)(THF)$.[1] Some bimetallic heteronuclear OUO-M (M = Mn, Fe and Co) complexes were obtained in their subsequent works.[2,3]

In the present work, we probe, using a relativistic DFT method, whether features of the pacman ligand can be exploited to obtain binuclear uranium complexes. Initially two uranyl groups were placed into the ligand cavity. Full geometry optimizations of $(UO_2)_2(L)$ led to two minimum-energy structures, which exhibit unusual coordination modes of uranyls: one is a T-shape formed by the two linear uranyls, and another – a Butterfly-shaped unit with one linear uranyl coordinating side-by-side to another cis-uranyl. The Butterfly-type $(U_2O_4)(L)$ not observed experimentally was found to be more stable than the T-shaped isomer for which experimental analogues are known. The formation of Butterfly and T-shaped complexes from the mononuclear $(UO_2)(H_2L)(THF)$ was found to be endothermic. The protonation and further dehydration of the two former are thermodynamically favorable, at least in the gas phase. As a possible product of them we have found a binuclear uranium(VI) complex having a O=U=O=U=O unit with an oxygen shared between the two uranyls.

[1]. P. L. Arnold, A. J. Blake, C. Wilson, J. B. Love, *Inorg. Chem.* **2004**, *43*, 8206.
[2]. P. L. Arnold, D. Patel, A. J. Blake, C. Wilson, J. B. Love, *J. Am. Chem. Soc.* **2006**, *128*, 9610.
[3]. P. L. Arnold, D. Patel, C. Wilson, J. B. Love, *Nature* **2008**, *451*, 315.

[P2-37]

Relationship Between the Electronic Property and the Corrosion Inhibition Activity of Some Organic Compounds

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The effect of structural properties on chemical activity for four compounds has been studied by some semi-empirical calculations. The correlation between the molecular structures and some calculated electronic properties has been investigated by using AM1 and PM3 SCF quantum chemical calculations, All structures of these compounds have been optimized, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), energy level and energy gap have been computed, and then the relations between the inhibition efficiency and all quantum chemical parameters have been discussed.

References:

1. M.A. Quraishi, M.A.W. Khan, D. Jamal, M. Ajmal, S. Muralidharan, S.V.K Lyer, J. Appl. Electrochem. 1996, 26, 1253.
2. M.A. Quraishi, M.A.W. Khan, D. Jamal, M. Ajmal, S. Muralidharan, S.V.K Lyer, Br. Corros. J., 1997, 32, 72.
3. F. Bentiss, M. Traisnel, M. Lagrenee, J. Appl. Electrochem. 2001, 31, 41.
4. I. Sheikhshoaie, F. Baghaei, A. Dadgarnezhad, Asian Journal of Chemistry, 2006, 18(3), 1903.
5. F. Baghaei, I. Sheikhshoaie, A. Dadgarnezhad, Asian Journal of Chemistry, 2005, 17(1), 224.
6. J.J.P. Stewart, MOPAC, a Semiemperical Molecular Orbital Program, in QCPE455, 1983, Vol. 6, p. 1990.

[P2-38]

Kohn-Sham Methods with Model Exchange-Correlation Potentials

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Most efforts in density functional theory (DFT) focus on designing density functional approximations while Kohn-Sham potentials play a supporting role. An appealing alternative to the conventional approach is to model Kohn-Sham potentials directly from Kohn-Sham orbitals. Given a Kohn-Sham exchange or correlation potential in analytical form, it is possible to reconstruct the parent energy functional up to a gauge transformation of the energy density. The main challenge for the potential-first DFT is to ensure that the model potential is a functional derivative of some density functional. We report recent progress in designing model Kohn-Sham potentials, give examples of density functionals reconstructed from approximate exchange-correlation potentials, and survey techniques for identifying model potentials that are not functional derivatives.

[P2-39]

Electronic structure and doping in ZnO bulk, slabs, and clusters

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Being a wide-gap semiconductor, the ZnO and its various doped forms emerged as a prominent material with potential applications in various fields of the optoelectronic industry. In an effort to reveal insights of its electronic structure a comparison is made between the characteristics of the bulk and slab solid models using periodic boundary conditions and some different sized cluster models at molecular level. First-principles calculations based on density functional theory (DFT) within the pseudopotential plane-wave method were performed on bulk and slabs of ZnO. Furthermore, high level ab-initio SCF and DFT calculations on smaller ZnO clusters were also performed, sustained by semiempirical calculations on a variety of doped and undoped clusters. The geometries, band structures, energies, and other electronic properties such as HOMO-LUMO gaps and band gaps were investigated and compared.

[P2-40]

Electronic Nature of a Self-Assembled ADADA Hydrogen-Bonded Helix

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Watson and Crick's observations of DNA in 1953 provided the motivation to develop synthetic molecules that could self-assemble into double-helical structures akin to DNA. Although several studies have achieved this goal via metal-ligand coordination,[1] fewer examples exist that exploit solely non-covalent interactions such as hydrogen bonding and aromatic stacking interactions. Of those examples that do exist, many of them are simply minor variations of the basic DNA scaffold, employing DNA analogues or derivatives. A recent experimental study on a self-associating non-DNA-based helix,[2] consisting of alternating hydrogen bond donor and acceptor groups, has led us to question the electronic nature of such a system. The current investigation examines the interactions that arise upon helix formation using electronic structure calculations and the theory of atoms in molecules (AIM). Analogous to a completed study on tuning the strength of AAA-DDD hydrogen-bonded complexes,[3] various functional group substitutions will be investigated to determine how the strength of binding is affected. Furthermore, the previous results from the AAA-DDD complexes allows for a comparison between hydrogen bonding present in coplanar systems versus the non-coplanar structure of the ADADA helix.

1. Albrecht, M., Chem. Rev. 2001, 101, 3457-3497.
2. Li, J. X.; Wisner, J. A.; Jennings, M. C., Org. Lett. 2007, 9, 3267-3269.
3. Newman, S. G.; Taylor, A.; Boyd, R. J., Chem. Phys. Lett. 2008, 450, 210-213.

[P2-41]

Towards an understanding of the dissociation mechanism of gas phase protein complexes

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Analyses of molecular dynamics calculations are presented that examine the dissociation of charged, gas phase protein complexes. Free energy profiles as a function of center of mass distance are calculated, and details of the unfolding and dissociation pathway for symmetrically and asymmetrically charged complexes is discussed.

[P2-42]

Towards understanding the dissociation mechanism of a weak acid in aqueous solution

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Understanding the dissociation mechanism of a weak acid in aqueous solution is of great importance not only for acid-base chemistry but also for understanding many biological processes. A detailed microscopic mechanism for weak acid dissociation in solution can only be obtained by finding and characterizing the intermediates of dissociation. As an important first step, we successfully explored the ability of hydrofluoric acid to produce dissociation intermediates using carefully designed first principles molecular dynamics simulations and characterize them using infrared spectroscopy by spectral decomposition technique based on maximally localized wannier orbitals. This is achieved by investigating the various compositions of amorphous mixtures of hydrogen fluoride and water at cryogenic conditions, favoring the formation of ion-pair dissociation intermediates to reach following conclusions. First, The broad "continuous" IR absorption ranging from 1000 to 3000 cm-1 shown by the cryogenic mixtures of HF and H2O are due to the presence of proton shared and ion-pair dissociation intermediates. The proton shared species are responsible for the intense absorption centered at 1800cm-1. Second, topology of first solvation shell determines the ionization and the asymmetric stretching frequency of shared proton of H2O.HF complex. Third, we are able to propose a mechanism of ionization by linking the first solvation shell pattern and degree of ionization. Fourth,A comparatively smaller magnitude of Nuclear quantum effects observed in this case shows that the local potential felt by hydrogen atoms in amorphous-phase proton-shared ion pairs is quasi-harmonic. Fifth, The shape of proton potentials for the three limiting structures are similar. Sixth, Long range electro static effects are small compared to the first solvation shell effect in determines the fate of ion-pair intermediates

1.Radu Iftimie, Vibin Thomas et al. Journal of the American Chemical Society 2008 130 (18), 5901
2.Vibin Thomas and Radu Iftimie. Journal of Physical Chemistry B 2009 113 (13), 4152

[P2-43]

Ground-State Green Fluorescent Protein Chromophore Z-E isomerization

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Green fluorescent protein (GFP) and other homologue fluorescent proteins (FPs) are widely used as markers in molecular and cellular biology. A number of FPs demonstrate photoswitching behaviour related to photoconversion of the chromophore from the fluorescent Z isomer to the non-fluorescent E isomer. This photobleaching process may be reversed by irradiation at a different (shorter) wavelength or thermally. Although the reversible photobleaching can be detrimental to the application of FPs as fluorescent probes, it may also lead to applications in photoswitching devices. Photoswitching of the FPs is a complex process involving the isomerization of the chromophore itself, and the rearrangement of the aminoacid residues around it. In this contribution, we will describe our approache to the theoretical study of the Z-E isomeriazation of the GFP chromophore on the ground-state potential energy surface. Ab initio and DFT electronic structure calculations as well as the molecular dynamics simulations with a newly developed force field parameters for the chromophore will be presented and the calculated free energy profiles will be used to discuss the possible mechanisms of the thermal fluorescence recovery in the phtobleached FPs.

[P2-44]

Monte Carlo atomic simulations with coordinate transformations.

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Traditional Monte Carlo simulations of molecular systems perform trial moves one atom at a time. When the motions of the atoms are highly correlated a "smarter" algorithm would move a group of closely interacting atoms instead. The potential energy surface of a system should provide enough information about connectedness of atoms. By transforming atomic coordinates into collective coordinates that take this connectedness into account, we can perform Monte Carlo step in collective coordinates and then invert the transformation to recover new atomic coordinates. This would result at a higher rate of acceptance and fewer simulation steps.

[P2-45]

The Effect of Multiplicity on the Structure of Iron (II) and Iron (II) Porphyrins

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The functionality of the hemoglobin protein involves the displacement of the iron atom from the porphyrin plane of the heme group. In this 'domed' geometry the iron atom is in the quintet state. It is generally believed that this geometry is a result of the high spin state of iron being more spatially extended than the lower spin states. Conversely, it has been shown that in isolated atoms the high spin state is spatially smaller than the low spin state of an atom with the same charge and configuration[1]. In this study the displacement of Fe^{2+} from the porphyrin plane in iron (II) porphyrin complexes is investigated with respect to the spin state of Fe^{2+}. Density functional theory, utilizing the 6-31G* basis set, is employed for calculations of Fe^{2+}, iron (II) porphyrin and imidazole ligated iron (II) porphyrin. Each molecule is calculated in the singlet (S=0), triplet (S=1), quintet (S=2), septet (S=3) and nonet (S=4) spin states. Various parameters associated with the central iron atom are investigated including atomic distances, volume and electron density.

1. Boyd, R. J. *Nature*, **1974**, 250(5467), 566-7.

[P2-46]

Monofluoridation and Difluoridation: Examing the Thermodynamic Effects of Added Nucleophiles on the Dimerization of Acyclic and Cyclic Dialkyldialkoxystannanes

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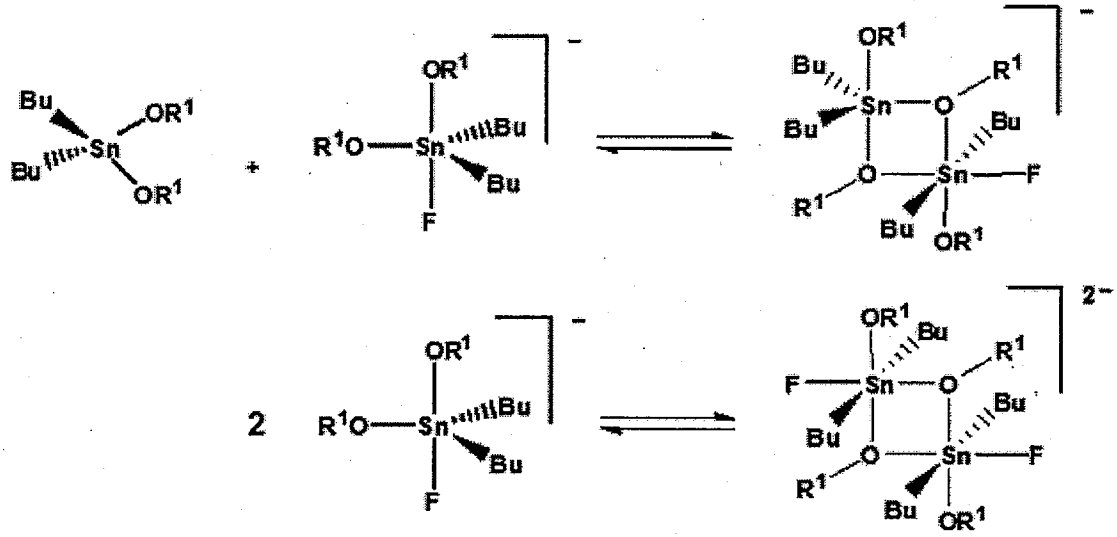
Tin-containing intermediates derived from diols and dialkyltin oxides, termed dialkylstannylene acetals, are widely used as intermediates to facilitate the regioselective monosubstitution of diols and polyols by electrophiles [1-3]. Nucleophiles, such as halide ions or tertiary amines, are often added to the reaction mixtures because they accelerate the reactions and sometimes alter the regioselectivity. The dialkylstannylene acetals exist as mixtures potentially containing monomers, dimers, and higher oligomers. We have examined the monomer-dimer equilibria for various acyclic and cyclic dialkyldialkoxystannanes, and have calculated the thermodynamics associated with monofluoridated and difluoridated dimerization reactions. The goal of our study is to use computational chemistry to try to understand how these nucleophiles influence the species that are present in the reaction mixtures, using fluoride as the added nucleophile, to shed light on the ambiguous mechanisms of these popular reactions. Substituent effects previously shown to influence nonfluoridated dimerization [4] are also explored examined in the present study. MP2 single point calculations were performed on geometries optimized using B3LYP, with the LANL2DZdp basis set with diffuse and polarization functions and its effective core potential for tin.



[1]. David, S.; Hanessian, S. *Tetrahedron* **1985**, *41*, 643-663. [2]. Grindley, T. B. *Adv. Carbohydr. Chem. Biochem.* **1998**, *53*, 17-142. [3]. David, S.; Thiéffry, A.; Veyrières, A. *J. Chem. Soc. , Perkin Trans. 1* **1981**, 1796-1801. [4]. Whittleton, S. R.; Rolle, A. J.; Boyd, R. J.; Grindley, T. B. *Organometallics* **2009**, Submitted.

[P2-47]

Vibrational states of H_2CO: A direct dynamics semiclassical initial value representation approach

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Semiclassical quantum dynamics techniques are of interest when approximate quantum effects are needed to properly describe the system under study. In particular, the semiclassical initial value representation (SC-IVR) is a useful method for conducting quantum dynamics, where the quantum time evolution operator is approximated by a semiclassical form that makes use of classical trajectories. Therefore, one can obtain quantum effects from a classical molecular dynamics simulation. Here, we present the energies of low-lying vibrational states of H_2CO calculated with SC-IVR using trajectories from direct dynamics simulations. They show a significant improvement to those determined from the harmonic approximation. We provide unique insight into the SC-IVR technique and discuss extensions to the method that will improve its utility for a variety of problems. The direct dynamics SC-IVR calculations were carried out with in-house computer programs that interface the Molecular Modelling Toolkit (MMTK) with well-known quantum chemistry software.

[P2-48]

Improving the safety of estrogen supplements by avoiding carcinogenic pathways

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Hormone supplements were widely used by post-menopausal women up until recently to relieve menopausal sympoms such as hot flashes, and to protect against osteoporosis, heart attack and stroke. However, extensive studies since 2003 have shown that long term use of the equine estrogens equilin and equilenin (present in the commercial drug Premarin) and probably the natural human female hormone estradiol as well, lead to an increased incidence of breast and uterine cancer. I will discuss two carcinogenic mehanisms which act synergistically, the metabolic formation of reactive quinones (tumor initiation) and the proliferative effect of ligands which are selective for estrogen receptor alpha (ERα). DFT calculations will be used to analyze the probability of quinone-forming pathways, and how to avoid them. Docking and scoring of test ligands for binding to the estrogen receptors ERα and ERβ will be carried out using MOE software(Chemical Computing Group). Over 70 molecules have been synthesized based on these calculations, many of which show binding affinities and estrogen potency superior to estradiol. Some of these molecules are being subjected to intensive testing to see whether they may offer a safer alternative to traditional hormone replacement therapy.

[P2-49]

DFT calculation of a polaron in DNA

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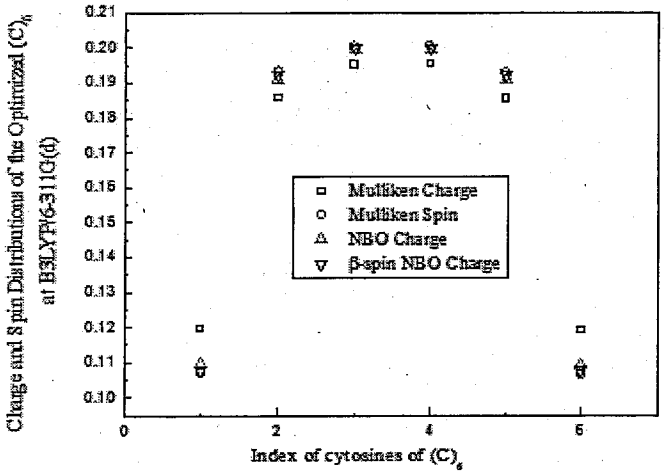
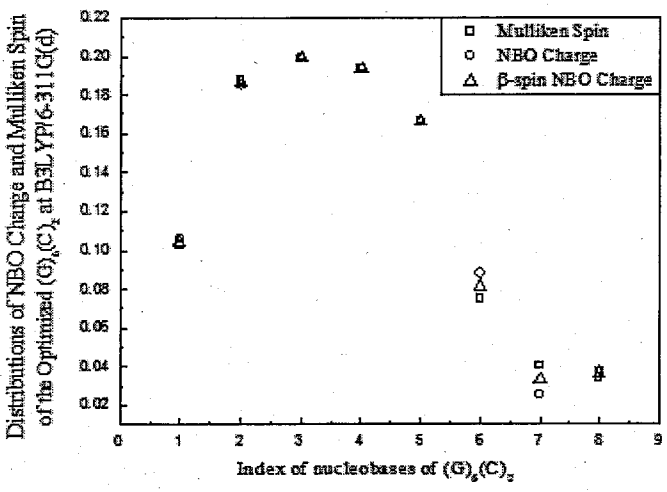
DNA is not only the carrier of genetic information, but also the medium of long range charge transfer in many biological processes, such as damage and damage detection in DNA. At present, the most widely accepted mechanism is the polaron mechanism, and calculations of polaron formation in DNA are mostly based on model Hamiltonians. In this work, ab initio density functional theory (DFT) has been used to investigate the polaron in DNA. The formation of a distortion polaron is discussed. The distortion polaron is generated by a geometrical distortion of DNA, such as the distance distortion and the twist angle distortion between two adjacent nucleobase pairs. Furthermore, how the sequence of nucleobases affects the DNA-mediated charge transfer in the polaron mechanism is also explored.





[P2-50]

Model core potentials for studies of scalar relativistic effects and spin-orbit coupling at Douglas-Kroll level. I. Theory and applications to Pb and Bi

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Theory of model core potentials that can treat spin-orbit coupling effects at the level of Douglas-Kroll formalism has been developed. By storing the damping effect of kinematic operator in the Douglas-Kroll spin-orbit operator into an additional set of basis set contraction coefficients, the Breit-Pauli spin-orbit code in the GAMESS-US program was successfully used to perform Douglas-Kroll spin-orbit calculations. It was found that minute errors in the radial functions of valence orbitals lead to large errors in the spin-orbit energy levels and thus fitting of the spin-orbit matrix elements is necessary in model core potential parameterization.

The first model core potentials that include the new formalism were developed for two 6p-block elements, Pb and Bi. The valence space of the 5p, 5d, 6s, and 6p orbitals was used because of the large spin-orbit coupling between the 5p and 6p orbitals. The model core potentials were validated by in the calculations of atomic properties as well as spectroscopic constants of diatomic metal hydrides. The agreement between results of the model core potential and all-electron calculations was excellent, with energy errors of hundreds of cm^{-1} and hundredths of eV, r_e errors of thousandths of Å, and ω_e errors under 20 cm^{-1}. Two kinds of interplay between spin-orbit coupling effect and bonding process (anti-bonding and bonding SOC) were demonstrated using spin-free term potential curves of PbH and BiH. The present study is the first extension of the model core potential method beyond Breit-Pauli to Douglas-Kroll spin-orbit coupling calculations.

[P2-51]

Applications and extensions of the source-sink potential approach

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For molecular conductors, the source-sink potential (SSP) Hückel model [1,2] provides a simple tool for the calculation of the electron transmission probability. Recently, the SSP method has been combined with graph theory, and criteria have been established [3] under which two different molecular electronic devices yield identical transmission probabilities. Since these criteria have been derived within the Hückel approximation, here we investigate their validity by performing Kohn-Sham density functional calculations. We find that some systems, predicted to be equiconducting at the Hückel level, remain equiconducting at the Kohn-Sham level while others do not. Explanations for the obtained discrepancies are provided. Furthermore, we present an extension of the SSP approach for the Hartree-Fock method, accounting for electron repulsion and exchange effects.

[1] M. Ernzerhof, J. Chem. Phys. 127, 204709 (2007).
[2] F. Goyer, M. Ernzerhof, M. Zhuang, J. Chem. Phys. 126, 144104 (2007).
[3] P. W. Fowler, B. T. Pickup, T. Z. Todorova, Chem. Phys. Lett. 465, 142 (2008).

[P2-52]

Fragments in molecules

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In the present study 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 makes it not only possible to decompose the deformation density, $\Delta\rho$, into the different components (such as σ,φ,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 the 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 thedescription of different types of chemical bonds. The applicability of the ETS-NOCV scheme is demonstrated for single (H3X-XH3, for X = C,Si, Ge, Sn) and multiple ($H_2X=XH_2$, H_3CXXCH_3, for X = C, Ge) covalent bonds between main group elements, for sextuple and quadruple bonds between metal centers (Cr_2 ,Mo_2 ,W_2, $[Cl_4CrCrCl_2]^{4-}$) and finally for double bonds between a metal and a main group element ($(CO)_5Cr=XH_2$, for X = C, Si, Ge, Sn).Applications are also given to hydrogen- and agostic bonds.

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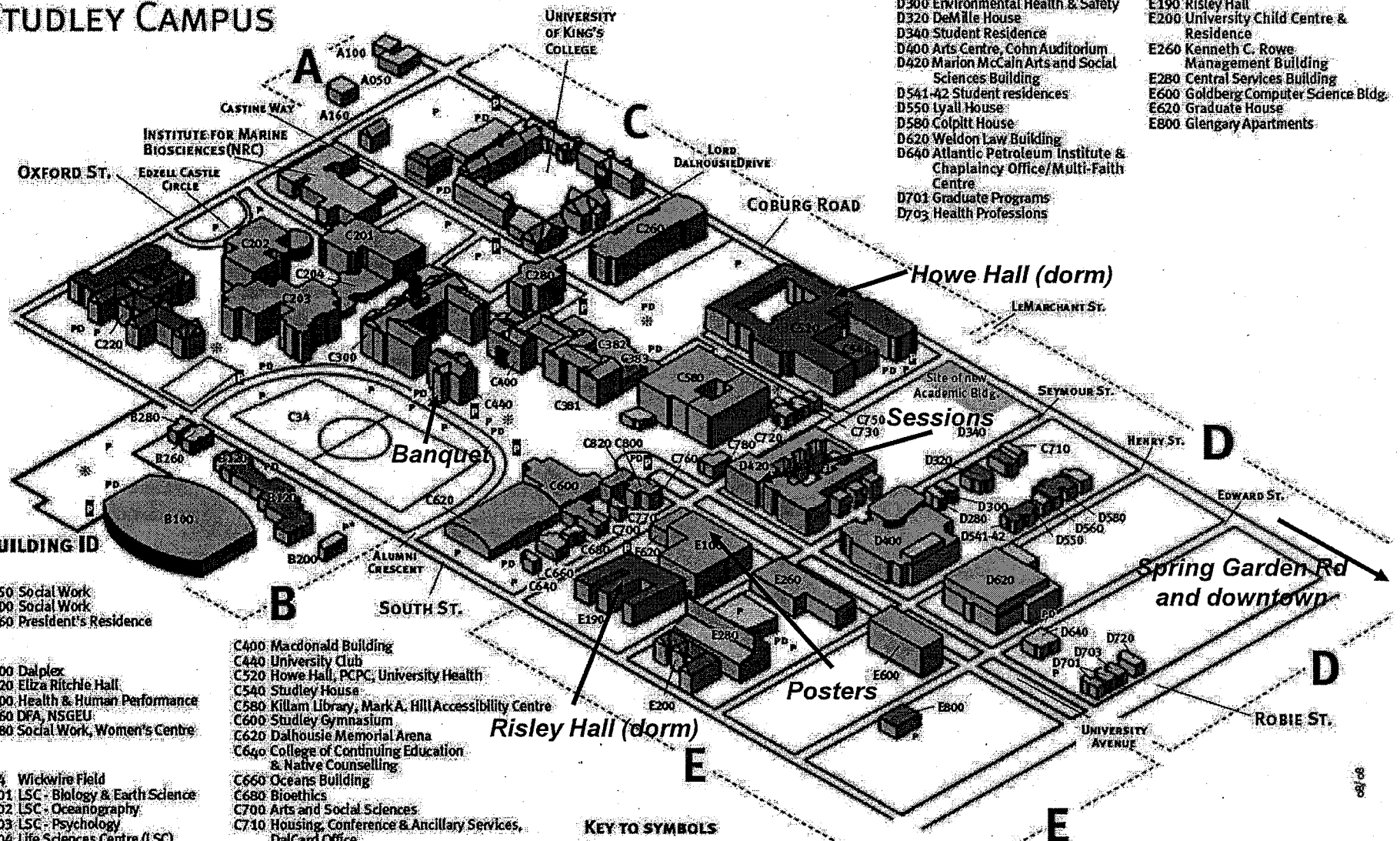
Maps of Dalhousie and Halifax

DALHOUSIE UNIVERSITY CAMPUS

STUDLEY • CARLETON • SEXTON

STUDLEY CAMPUS



BUILDING ID

A
A050 Social Work
A100 Social Work
A160 President's Residence

B
B100 Dalplex
B120 Eliza Ritchie Hall
B200 Health & Human Performance
B260 DFA, NSGEU
B280 Social Work, Women's Centre

C
C34 Wickwire Field
C201 LSC - Biology & Earth Science
C202 LSC - Oceanography
C203 LSC - Psychology
C204 Life Sciences Centre (LSC)
C220 Shirreff Hall
C260 Sir James Dunn Building
C280 Chase Building
C300 Henry Hicks Building
C381, C382 Chemistry,
C383 Chemical Storage Facility
C400 Macdonald Building
C440 University Club
C520 Howe Hall, PCPC, University Health
C540 Studley House
C580 Killam Library, Mark A. Hill Accessibility Centre
C600 Studley Gymnasium
C620 Dalhousie Memorial Arena
C640 College of Continuing Education & Native Counselling
C660 Oceans Building
C680 Bioethics
C700 Arts and Social Sciences
C710 Housing, Conference & Ancillary Services, DalCard Office
C720 European Studies
C730 APICS, Science Co-op
C750 Transition Year Program
C760, C800, C820 Economics
C770 1252 LeMarchant
C780 Arts and Social Sciences

D
D280 Nu-Tech
D300 Environmental Health & Safety
D320 DeMille House
D340 Student Residence
D400 Arts Centre, Cohn Auditorium
D420 Marion McCain Arts and Social Sciences Building
D541-42 Student residences
D550 Lyall House
D580 Colpitt House
D620 Weldon Law Building
D640 Atlantic Petroleum Institute & Chaplaincy Office/Multi-Faith Centre
D701 Graduate Programs
D703 Health Professions

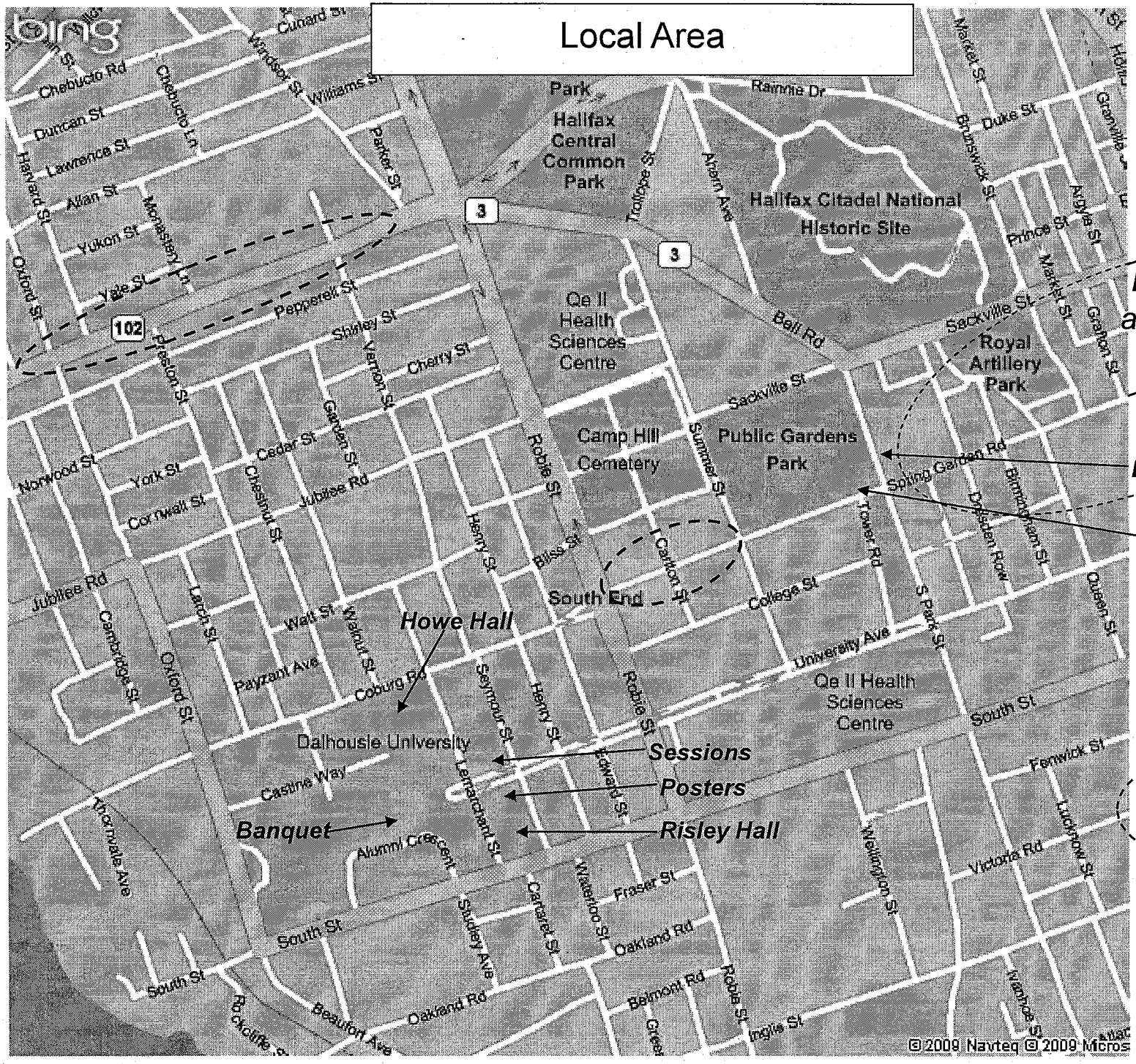
E
E100 Student Union Building (SUB)
E190 Risley Hall
E200 University Child Centre & Residence
E260 Kenneth C. Rowe Management Building
E280 Central Services Building
E600 Goldberg Computer Science Bldg.
E620 Graduate House
E800 Glengary Apartments

KEY TO SYMBOLS

P — Permit Parking
P — Metered Parking
PD — Parking for people with disabilities
✻ — Emergency "Code Blue" Phone

08/08

Local Area


Halifax Central Common Park
Halifax Citadel National Historic Site
Qe II Health Sciences Centre
Royal Artillery Park
Camp Hill Cemetery
Public Gardens Park
South End
Howe Hall
Dalhousie University
Qe II Health Sciences Centre
Sessions
Posters
Risley Hall
Banquet
Downtown and harbour
Lord Nelson Hotel
Airporter stop
Restaurants and Shops
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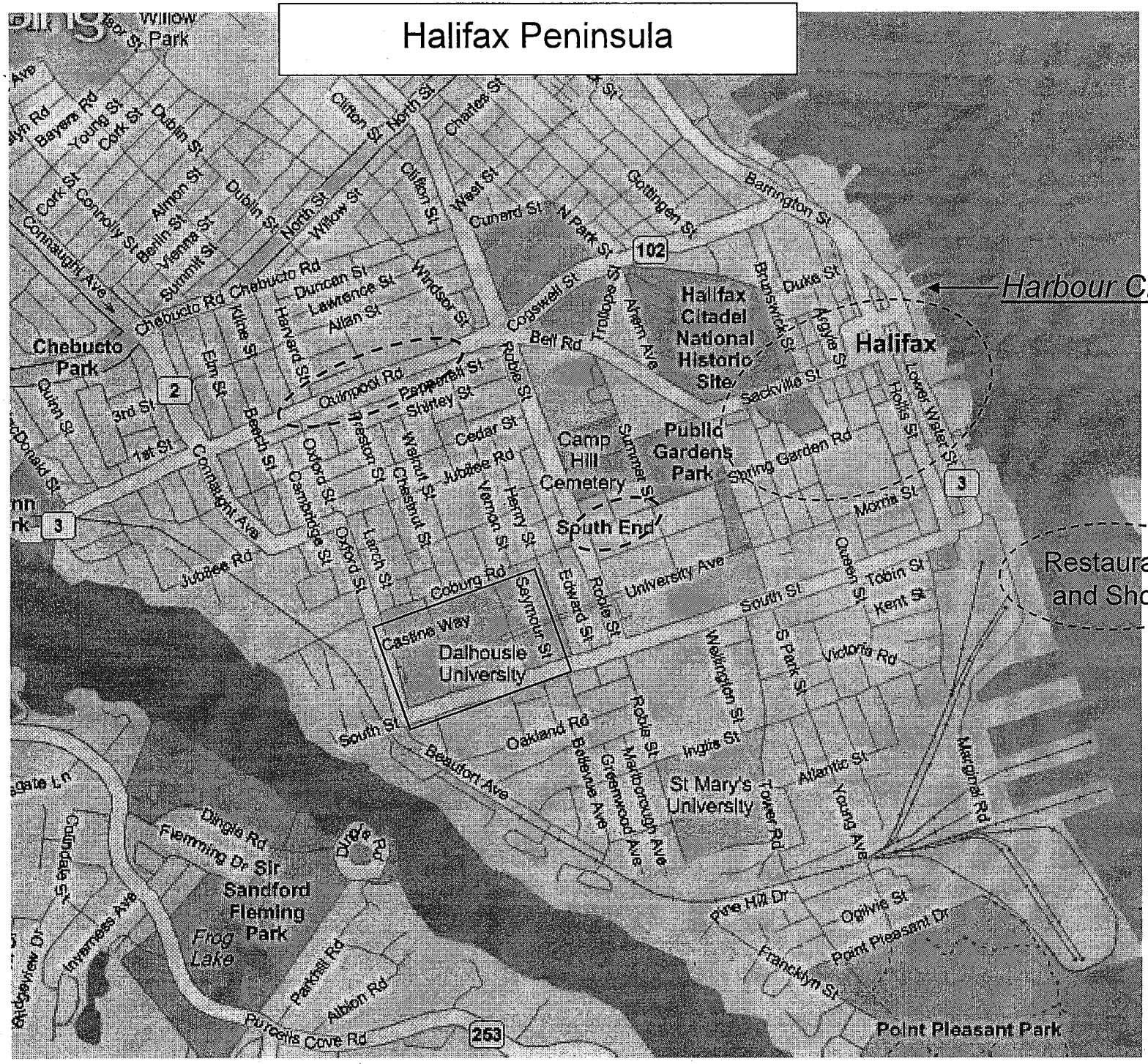
Halifax Peninsula



← *Harbour Cruises*

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