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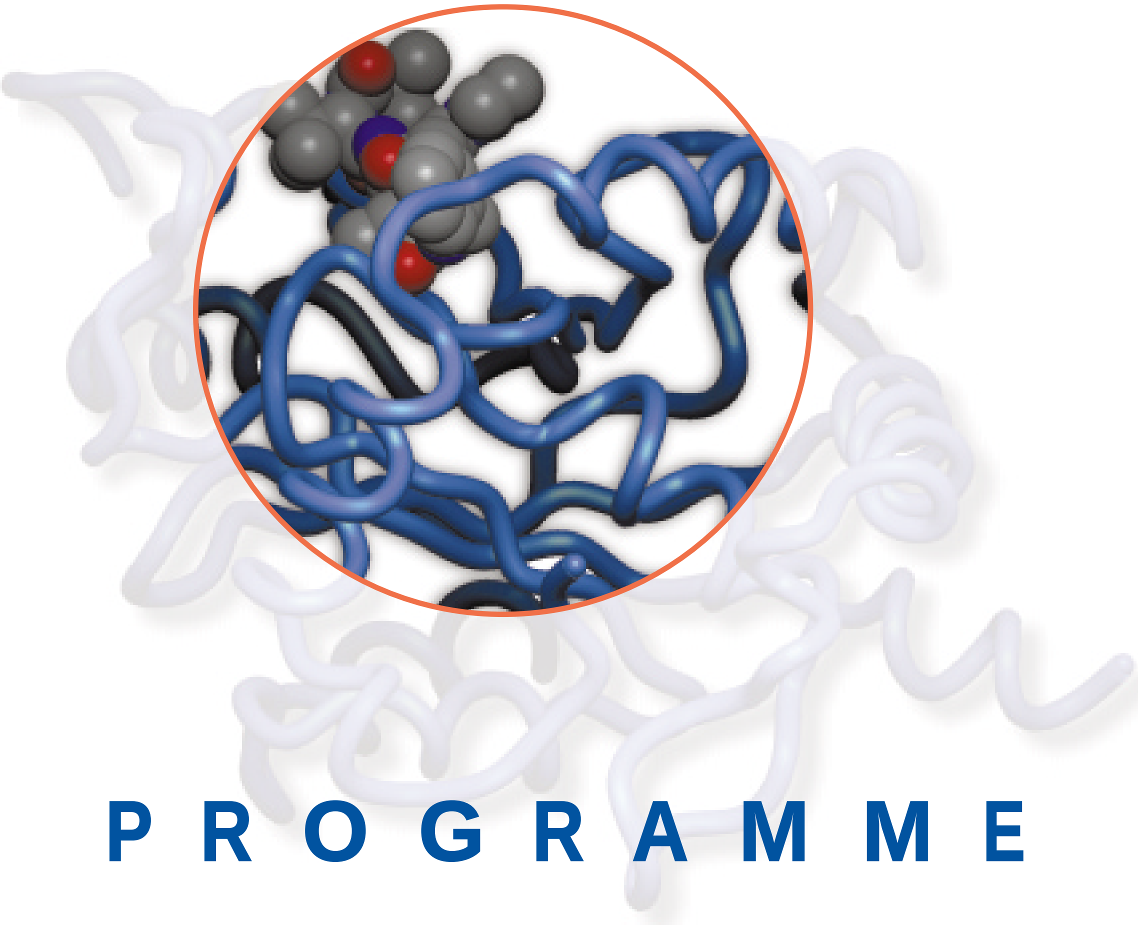

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INVITED TALKS

Rodney J. Bartlett

Ab Initio Density Functional Theory

Rodney J Barlett, Stanislav Ivanov, So Hirata, Ireneusz Grabowski, University of Florida, Gainesville, Florida 32611-8435, USA

There is a fundamental dilemma in current density functional theory (DFT) methods, in that there is no way to converge to the right answer. This is contrary to the well-known paradigm of correlated ab initio methods. In this respect, DFT is a ‘semi-empirical’ theory and does not have systematic ways for improvement. We propose ab initio DFT to help resolve this problem. Taking functional derivatives with respect to density of exchange and correlation energy expressions, we introduce local, multiplicative one-particle operators that account for these terms. We have developed an exact exchange theory for molecules and are developing correlation potentials that can be tied to MBPT(2), MBPT(3), or even coupled-cluster theory. Even at the exchange only level (order of magnitude larger than correlation), many interesting, and more accurate results occur.

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David A. Case

Generalized Born Models of Macromolecular Solvation Effects

Department of Molecular Biology, The Scripps Research Institute, La Jolla, CA 92037

It is often useful in computer simulations to use a simple description of solvation effects, instead of explicitly representing the individual solvent molecules. Continuum dielectric models often work well in describing the thermodynamic aspects of aqueous solvation, and approximations to such models that avoid the need to solve the Poisson equation are attractive because of their computational efficiency. I will discuss on approach, the generalized Born model, which is simple and fast enough to be used for molecular dynamics simulations of proteins and nucleic acids. Strengths and weaknesses will be discussed, both for fidelity to the underlying continuum model, and for the ability to replace explicit consideration of solvent molecules in macromolecular simulations. The focus will be on versions of the generalized Born model that have a pairwise analytical form, and therefore fit most naturally into conventional molecular mechanics calculations.

David Clary

Quantum diffusion Monte Carlo simulation of hydrated clusters and proteins

Department of Chemistry, University College London, 20 Gordon St, London WC1H OAJ, UK

This talk will describe recent calculations we have performed on the vibrational ground states of molecular clusters using the quantum diffusion Monte Carlo method. Results on water clusters, clusters of benzene and phenol with water molecules, hydrated DNA bases and model proteins demonstrate the importance of using quantum mechanics to treat vibrational zero-point energy and wide amplitude motion in these weakly-bound systems.

NOTES

Toshikazu Ebisuzaki

Towards Real-time and Interactive Simulations of Million Atom Systems

Toshikazu Ebisuzaki, Tetsu Narumi, Ryutaro Susukita, Hideaki Furusawa,
Atsushi Suenaga, Noriaki Okimoto, Takahiro Koishi, and Kenji Yasuoka*

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Simulating millions of atoms in a real-time and interactive way, and playing the game of molecular dynamics in a 3D-visualization system is the final goal of our research project. We believe that it should lead to major breakthroughs at the frontiers of science by combining the imagination of scientists and the computational power of machines. A great step towards this goal will be completed at the end of the year 2000, that is, the development of a special-purpose computer named Molecular Dynamics Machine (MDM), which will have the peak performance of 100 Tflops and a realistic performance of 30 Tflops, which means the CPU time of 0.19 seconds per time step for molecular dynamics simulation of a million particles with the Ewald method. It will be more than ten times faster than the currently available fastest supercomputer in the world. In this talk, I will introduce the details of the architecture and performance of the MDM together with its two promising applications: the crystal nucleation and growth in molten salts and the refolding of proteins in solvent.The crystal nucleation and growth in molten NaCl has been studied by performing molecular dynamics simulations on a small subset of the MDM machine. In the simulations, 13824 ions were equilibrated for 500,000 steps or 1 (ns) at the liquid sate of 1100 (K), then quenched to the solid state, and equilibrated for 500,000 steps at this temperature. The outstanding speed of the MDM has made it possible for the first time to simulate such a large system readily. The CPU time of the MDM for one time step was 0.5 (s), which is thousand times shorter than that of a SUN workstation (UltraSPARC-II 400MHz). It was computationally observed that if the size of a nucleated solid cluster is larger than a critical value, the cluster grows to the single crystal or to the polycrystall depending on the process of cooling. The refolding process of small and middle-size proteins has been studied by performing molecular dynamics simulations with explicit dynamics of solvent molecules on Fujitsu supercomputer VPP700E/160 at RIKEN, and it was found for the first time that the protein folding can be divided into three phases. Firstly, an alpha-helix is developed from a beta-turn through the state of 3_10-helix in the alpha-helix phase. Secondly, proteins become compact, and tertiary structures are formed in the packing phase. Finally, a beta-sheet is developed by the one-by-one formation of hydrogen bonds between two cohered strands in the beta-sheet phase. Although these preliminary calculations are performed on a “conventional” supercomputer, the results are very interesting and inspiring; we will soon learn much more from the simulations with the MDM.

NOTES

Eugene Fluder

Latent Semantic Structure Indexing (LaSSI)

Eugene Fluder, Jr, and Richard Hull, Merck Research Laboratories, Box 2000, RY50SW-100, Rahway, NJ 07065-0900

A novel extension of the vector space model for computing chemical similarity called Latent Semantic Structure Indexing (LaSSI) is described. This method uses the singular value decomposition (SVD) of a molecule/descriptor matrix to create a low dimensional representation of the original descriptor space. Each new dimension represents correlated descriptors in the original space, which can be thought of as latent chemical "concepts". Ranking compounds based upon the similarity of these concepts versus the similarity of their original descriptors has several advantages: concept matching is less brittle than descriptor matching; choice of the number of singular values provides rational fuzzying of the search; probes created from more than one molecule are well tolerated; and the reduction in the dimensionality of the chemical space increases processing speed. A discussion of the LaSSI method and its advantages in the context of searching large chemical databases will be presented.

William A. Goddard

New methods for de novo Simulations and applications to Catalysis, Materials, and Biochemistry

California Institute of Technology (139-74), Pasadena, CA 91125

Advances in theory and methods are making it practical to consider fully first principles (de novo) predictions of many important systems and processes in the Chemical, Biological, and Materials Sciences. Indeed such de novo atomistic simulations will likely revolutionize both the mode for doing the science and the nature of industrial applications, where quantitative models will eventually become the basis for design and operations. *Critical to de novo simulations is to base all predictions on first principles quantum mechanics*. However, many applications require scales of size, length, and time greatly exceeding the capabilities of current quantum methods. Thus de novo simulations require the development of a hierarchy of methods rigorously basing the results on quantum mechanics while allowing the description of much larger length and time scales.

We will describe recent advances relevant to such developments including:

- Quantum Chemistry including solvation and Force Field Embedding (QM/MM)
- De novo Force Fields to describe reactions and phase transitions
- Molecular dynamics including solvation and describing polymerization and growth
- Nonequilibrium molecular dynamics to describe rheology, thermal conductivity and other nonequilibrium processes
- Mesoscale simulations for the long length scales of processes such as gas diffusion in polymers and impurity diffuison in semiconductors.

We will summarize some recent applications of these methods to catalysis, materials science, and biochemistry to provide some flavor for the opportunities in applying such de novo methods. Applications to be covered will be selected from:

- Homogeneous polymerization catalysts (Grubbs Ru Metathesis, Brookhart poly-imine)
- Catalytic Activation of Small Alkanes (Mixed metal oxide selective oxidation, Catalytica $PtCl_2$ bisdiazene catalyst)
- Chemisorption and reforming of hydrocarbons on group VIII metal surfaces
- Mechanism of decomposition of high energy molecules (RDX, HMX)
- Plasticity, dislocations, and spall failure in metal alloys
- Nanotechnology, Nanorheology
- First principles predictions of Protein structure and protein folding rates

Thomas A. Halgren

Extending the OPLS-AA force field for ligand functionality

Thomas A. Halgren, Robert B. Murphy, George A. Kaminski, William L.Jorgensen,
and Richard A. Friesner

Accurate coverage of the full range of pharmaceutically relevant chemical structure is a daunting task. To address this important objective, we have sought to combine the best features of OPLS-AA and MMFF94. To this end, the extended OPLS-AA force field uses charge and van der Waals parameters validated in OPLS-AA liquid-phase simulations in conjunction with torsional and charge parameters derived from high-quality ab initio data. These data include the MMFF94 data, recomputed at higher quantum levels, plus extensive sets of data generated at Merck to extend the MMFF force field or generated at Columbia University to improve the OPLS-AA force field for peptides and proteins. The status of this effort will be summarized with emphasis on choices of functional form and procedures being developed to derive electrostatic and torsion parameters.

Sharon Hammes-Schiffer

Theoretical Perspectives on Proton-Coupled Electron Transfer Reactions

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University Park, PA 16802

A theoretical formulation of proton-coupled electron transfer (PCET) reactions in solution will be presented. This formulation is based on a multistate continuum theory, in which the solute is described with a multistate valence bond model, the solvent is represented as a dielectric continuum, and the active electrons and transferring protons are treated quantum mechanically. This formulation is a multidimensional extension of standard Marcus theory for single electron transfer. For PCET, the free energy surfaces are approximate paraboloids and depend on two solvent coordinates corresponding to the proton and electron transfer reactions. In this theoretical framework PCET reactions are described as transitions among these two-dimensional paraboloids. The free energy surfaces provide important information about the reaction mechanisms, such as whether the charge transfer reactions are concerted or sequential and, in the latter case, the order in which the charge transfer reactions occur. Rate expressions have been derived in the various limits. Theoretical predictions of the dependence of the rates, mechanisms, and kinetic isotope effects on the physical properties of the solute and the solvent will be discussed. The application of this theory to experimentally studied photoinduced PCET through asymmetric salt bridges will also be presented.

Anton Hopfinger

Applications of the 4D-QSAR paradigm to molecular similarity and virtual screening

Anton J. Hopfinger, José S. Duca and Yufeng Tseng, Laboratory of Molecular Modeling and Design (M/C-781), College of Pharmacy, University of Illinois at Chicago, 833 South Wood Street, Chicago, IL, 60612-7231, USA

The 4D-QSAR paradigm provides a vehicle to package molecular information into a set of descriptors as a function of conformation, alignment and atomic composition. The set of 4D-QSAR descriptors can be used by themselves, or in tandem with other descriptors, for the characterization of molecular similarity. The descriptors can also be transformed into 4D-QSAR models using ancillary training set data, and employed for virtual screening of compound libraries. The 4D-QSAR paradigm permits absolute (alignment-independent) and relative (alignment-dependent) molecular similarity comparison measurements. Further, molecular similarity comparisons can also be made as a function of substructures and/or atom-types composing the test compounds. 4D-QSAR virtual screens permit both the convergence and optimization of descriptor information in the estimation of an activity or similarity measure. An overview of the 4D-QSAR paradigm will be presented along with examples of applying the 4D-QSAR paradigm to both molecular similarity and virtual screening.

Peter Kollman

Entering the Era of Structure and Free Energy with Non Additive Force Fields

University of California, San Francisco

We will present recent results using a combined explicit/continuum model MM-PBSA(molecular mechanics-Poisson Bolzmann surface area) in simulating the free energies of complex biomolecular systems, giving examples from proteins, nucleic acids and cyclodextrin\complexes. We will then summarize where we stand in developing a general non-additive force field with off center charges for proteins, nucleic acids and organic molecules.

Paul Labute

A Widely Applicable Set Of 2_ D Descriptors

Paul Labute, Chemical Computing Group Inc., 1010 Sherbrooke Street West, Suite 910; Montreal, Quebec; Canada H3A 2R7, http://www.chemcomp.com

Three sets of molecular descriptors computable from connection table information are defined. These descriptors are based upon atomic contributions to van der Waals surface area, log P (octanol/water), molar refractivity and partial charge. The descriptors are applied to the construction of QSAR/QSPR models for boiling point, vapor pressure, free energy of solvation in water, solubility in water, Thrombin/Trypsin/Factor Xa activity, blood-brain barrier permeability and compound classification. The wide applicability of these descriptors suggest uses in QSAR/QSPR, combinatorial library design and molecular diversity work.

Daniel Lidar

Universal Fault Tolerant Quantum Computation On Decoherence-Free Subspaces.

University of California, Berkeley, USA.

Quantum computation is an exciting new field which promises dramatic computational advances, such as exponentially faster simulations of quantum mechanics, polynomial-time factoring, and fast database searches. However, quantum computers are very fragile and must be protected from unwanted interactions with their environment (the "decoherence problem"). The first half of the talk will be an introduction to this subject. In the second half a solution to the decoherence problem will be presented. Decoherence-free subspaces (DFSs) are "quiet corners" of the Hilbert space of a quantum system coupled to an environment. We developed the theory of DFSs, and recently found a general scheme to perform universal quantum computation fault-tolerantly on a DFS. This scheme has the important simplifying properties that (i) at most two-body interactions are required, and (ii) the system remains within the DFS throughout the entire implementation of a quantum logic-gate. The quantum computer is thus completely shielded from decoherence. Applications include several recently proposed solid-state quantum computer implementation, such as spin-spin coupled quantum dots.

NOTES

Ingo Muegge

Knowledge-based scoring – what makes the difference?

Ingo Muegge, Bayer Research Center, 400 Morgan Lane, West Haven, CT 06516

PMF-scoring has now been established as an alternative scoring approach for protein-ligand complexes with known 3D structure. Employed in molecular docking experiments, knowledge-based scoring functions have been shown to perform surprisingly well in identifying correct binding modes of protein-ligand complexes, in ranking protein-ligand complexes according to their binding affinities, and finding weakly binding molecules in large databases of small molecules. The designs of knowledge-based scoring functions differ in the definition of reference states and also in the treatment of intra-ligand interactions. New aspects of the PMF-scoring function are presented here that include a discussion of the ligand volume correction factor and possible reference states of the PMF-scoring function. In addition, a comparative study of docking/scoring experiments is presented based on MMP-3 inhibitors using DOCK4 with energy scoring and PMF-scoring as well as FlexX.

Dennis Newns

Molecular Dynamics and Protein Folding in the Blue Gene Supercomputer

Marc Snir, Blake Fitch, Wilm Donath, Maria Eleftheriou, Robert Germain, Susan Hummel, Dennis Newns, Ajay Royyuru, Bill Swope, George Almasi, Fran Allen, Jose Castanos, Calin Cascaval, Martin Casado, Mark Giampapa, Howard Ho, Elie Krevat, Albert Lee, Derek Lieber, Jose Moreira, Hank Warren, Dan Beece, Terry Bright, Monty Denneau, Ruud Haring, Peter Hochschild, Kiran Maturu, Rick Rand, and Nagesh Vishnumurti
IBM T.J. Watson Research Center, P.O.B. 218, Yorktown Hgts., NY 10598

There is a range of Biomolecular Processes which are relatively slow on the scale of atomic fluctuations. A well-known and studied example is protein folding. Such real time processes can be studied by Molecular Dynamics. It can be estimated that an adequate treatment of folding of even a small, fast folding protein by Molecular Dynamics requires a computer power of order 1015 floating point operations per second, or 1 petaflop. The Blue Gene supercomputer is a replicated single chip architecture with 32 1 Gflop processors, memory, and communications subsystems on a single chip; with 32000 chips 1 petaflop is achieved. We discuss what algorithms are appropriate for MD in this extremely parallel architecture, the implementation of multitrajectory small protein folding studies, and progress to date.

Anthony Nicholls

Poisson-Boltzmann Contributions to Protein-Ligand Binding

Poisson-Boltzmann (PB) theory attempts to account for the polar nature of water by representing it as a continuum of high dielectric. Solutes, whether small, drug-like molecules or proteins, are then represented as low dielectric shapes. The theory has shown good correspondence in reproducing the electrostatic component of all atom simulations but with much greater efficiency. One of the goals of PB research is to evaluate its utility in predicting the electrostatic component of protein-ligand binding. Despite some limited success, wide-spread adoption of such a procedure has been hampered by difficulties in use of PB codes, slow (relative) speeds of such and uncertainty as to the correct parameters for proteins. In this talk I will summerise the current status of this research, indicating successes and failures, and in particular our attempts to remove the procedural difficulties in obtaining rapid estimates of binding energies.

David A. Pearlman

The leap from precision to speed: New methods for drug design and database screening based on explicit and effective free energy grids.

Free energy simulations (free energy perturbation, thermodynamic integration) have long been considered the sin non quo of methods that can be used to determine relative binding energies. Unfortunately, these simulations are much too slow and cpu intensive to be useful in preliminary and interim stages of drug design. A new method has been developed, based on the OWFEG method (one window free energy grid), that incorporates some of the strengths of free energy simulations into a grid-based rapidly evaluable function suitable for use in high throughput database screening. Results using this method are promising. Overall, for the systems examined (IMPDH, p38, HIV protease), the OWFEG grid performs better than any of the commonly used scoring functions tested. We also demonstrate that in cases where high precision is required and high throughput is not, explicit free energy simulations are still the method of choice. Finally, we demonstrate a new, very simple function based on newly parameterized pairwise potential and suface area terms that can be used to prune large databases to yield a subset with a much higher fraction of “hits”. This function has been parameterized against binding and solubility data and so the derived parameters include an effective free energy component. Given its simplicity, this function is surprisingly good and begs reconsideration of suitability of functions that achieve comparable (or lesser) results with significantly more complex models.

Otto F. Sankey

Probing new materials and new material systems theoretically.

Department of Physics and Astronomy, Arizona State University, Tempe AZ 85287-1504

There is a large global effort to synthesize new crystalline materials and new material systems. ASU has an active experimental effort in this area which covers a range of systems and techniques, including the use of high pressure. We will describe what theoretical atomistic quantum mechanical (DFT) calculations can contribute to this exciting field. Examples of projects that will be described include high-pressure Ge-Nitride synthesis, high pressure crystallized “beer bubbles” (polymeric CO2 solids), and open framework semiconductors for electronic and thermoelectric applications.

Jeremy M Schofield

Efficient ab-initio simulation methods for reactive systems.

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A serious impediment to using ab-initio potential energy functions in simulations is the significant expense in their evaluation which severely limits the length of simulations. As the quality of the statistics obtained from simulation is greatly dependent on the length of the simulation, the uncertainties in averages obtained in many ab-initio simulations are quite large. The problem is particularly severe for processes that occur infrequently, as in the case of chemical reactions or slow conformational changes. We present an importance sampling method based upon a classical model which reduces the uncertainties in averages obtained in ab-initio simulations of reacting systems by orders of magnitude. The method is illustrated for hydrogen-bonded systems in which proton-transfer reactions occur.

NOTES

John S. Tse

Structural stability, phonon resonant scattering and thermolectric power of semi-conductor clathrates.

John S. Tse, Zhiqiang Li, Roger Rousseau and Kentaro Uehara, Steacie Institute for Molecular Scieces, National Research Council of Canada, Ottawa, Ontario, Canada

Recently, metal-doped semi-conductor clathrates have been suggested as potential candidates for high efficiency thermolectric materials due to their anomalously low and glass-like thermal conductivity behaviour [1]. In this presentation, the stability of these unusual clathrate structures will be examined with a real space method based on the scaled-second moment of the electron density of states [2]. This method allows the rationalization of the stability of a crystalline material from its basic local structural motifs [3]. We will show that the transfer of metal electrons to the semiconductor framework stabilizes the formation of the pentagon rings in the structure [4]. A resonant scattering model [5,6] is proposed to explain the thermal conductivity anomaly. Perturbative calculations on analogous clathrate hydrates show that even the guest-host interactions are small, symmetry forbidden crossings of localized guest vibrations and that framework acoustic branches are responsible for the scattering of the thermal phonons thereby increasing their thermal resistivity. First Principles calculations of the phonon band structures of selected metal-doped semi-conductor clathrates confirm this proposal. Finally, the thermopower of the clathrates is rationalized from the topology of the electron density of states near the Fermi level.

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Gennady M. Verkhivker

Hierarchy of energy models in understanding molecular recognition mechanisms

G. M. Verkhivker, D. Bouzida, D. K. Gehlhaar, P. A. Rejto, L. Schaffer, S. Arthurs, A.B. Colson, S.T. Freer, V. Larson, B.A. Luty, T. Marrone, P. W. Rose, Agouron Pharmaceuticals, Inc., A Warner-Lambert Company, 10777 Science Center Drive, San Diego, CA 92121 USA

Analysis of the common successes and failures in structure prediction of ligand—protein complexes with different structure prediction strategies and energy functions, allows establishing fundamental connections between topology of the binding energy landscapes and the results of docking simulations. Misdocked predictions in ligand—protein docking are classified as `soft' and `hard' failures. While a soft failure arises when the search algorithm is unable to find the global energy minimum corresponding to the crystal structure, a hard failure results from a flaw of the energy function to qualify the crystal structure as the predicted lowest energy conformation in docking simulations. We find that neither the determination of a single structure with the lowest energy nor finding the most common binding mode is sufficient to predict crystal structures of the complexes, which belong to the category of hard failures. In a proposed hierarchical approach, structural similarity clustering of the conformations, generated from equilibrium simulations with the simplified energy function, is followed by energy refinement with the more detailed force field. This protocol, that involves a hierarchy of energy functions, resolves some common failures in ligand—protein docking and detects crystallographic binding modes that were not found during docking simulations. Computer simulations of HIV-1 binding dynamics and thermodynamics has been performed for the SB203386 inhibitor with ensembles of protein conformations and allowed to incorporate protein flexibility effects and complement a structure—based experimental analysis of the inhibitor resistance to HIV-1 protease mutants. We have adapted a hierarchy of simplified and detailed energy functions to describe the topology of the binding energy landscape and adequately characterize the energetics of the binding modes. Simulations with ensembles of multiple proteins provides insights into the relationship between distribution of the inhibitor binding modes and corresponding families of protein conformational fluctuations. Thermodynamic analysis of SB203386 binding with HIV-1 protease mutants shows that the molecular origins of the inhibitor resistance can be in part rationalized based on the entropy and enthalpy contributions of the interaction energetics.

David M. Wardlaw

“Rate Theory for Barrierless Reactions: Improved Theory, More Applications, and New Software”

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A completely general canonical and microcanonical variational transition state theory expression for the rate constant has been derived for an arbitrary choice of reaction coordinate. The derivation is rigorous within the framework of Wardlaw- Marcus flexible transition state theory (FTST) and replaces earlier treatments which implicitly involved some significant assumptions. The rate expressions apply to any definition of the separation distance between fragments in a barrierless recombination (or dissociation) that is held fixed during hindered rotations at the transition state, and to any combination of fragment structure (atom, linear top, nonlinear top). The variational minimization of the rate constant with respect to this definition can be regarded as optimizing the reaction coordinate. The expression is analytic except for a configuration integral whose evaluation generally requires numerical integration over internal angles (from one to five depending on the fragment structures). The form of the integrand in this integral has important conceptual and computational implications. The talk will begin with a short tutorial on the distinguishing features of rate theory for association/dissociation reactions having no potential energy barrier between reactants and products. The theoretical developments described above will then be summarized. The remainder of the talk will focus on applications to selected radical recombination reactions with an emphasis on the effect of optimizing the reaction coordinate on the value of the rate constant, and on the physical siginificance of the optimized reaction coordinate itself. The improved version of FTST is a significant component of the recently released VariFlex software package for calculating the pressure and temperature dependence of barrierless reaction rates.

POSTERS

Hakima Abou-Rachid

Chemical Reactivity Control using Laser-Induced Dissociation Quenching and Alignment.

Hakima Abou-Rachid, T.Tung Nguyen-Dang and Osman Atabek, Département de Chimie, Université Laval, Québec G1K7P4, Qc, Canada,
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Intense laser fields may exert important forces on a molecular system leading to major alterations of its external and internal dynamics. Molecular alignment and orientation as well as bond softening and stabilization mechanisms offer the possibility of laser assisted molecular manipulation and reactivity control scenarios. This article examines such a control scheme based on a trapping effect, in strong infrared fields, recently described in 1D models (frozen rotation) as a dynamical dissociation quenching (DDQ) and its possible 2D extension to rotating molecules. It is particular shown, how, with an appropriate choice of laser parameters (frequency, intensity and phase), combined with a specific preparation of the molecular initial state, photodissociation can be controlled. H2+ molecular ion and its isotope HD+ are taken as illustrative examples.

J. Autschbach

Density Functional Calculations of NMR Spin-Spin Coupling Constants for Heavy Atom Systems

J. Autschbach and T. Ziegler Department of Chemistry, University of Calgary,
Calgary, Alberta, Canada T2N 1N4

The development of efficient ways to predict properties such as NMR parameters of systems containing heavy elements is one of the major goals of contemporary quantum chemistry. During the last decade, it has been demonstrated that NMR spin-spin coupling constants are computationally accessible by means of nonrelativistic functional theory for a largevariety of molecules containing 1st to 3rd row main group as well as 3d transition metal elements. However, for couplings involving heavy nuclei like ^{183}W, ^{195}Pt, ^{199}Hg or ^{207}Pb, a relativistic approach is absolutely necessary due to the dramatically large relativistic effects on the coupling constants, which depend on features of the wavefunction very close to the nuclei. We present a density functional formalism for the efficient computation of NMR spin-spin coupling constants based on the ZORA relativistic method. The most important terms arising in this formalism were implemented into the ADF density functional program and applied to 6th row main group and 5d transition metal systems. The results are very promising, but also indicate that for some systems higher orders might be important.

Fuqiang Ban

Theoretical Studies of the Antitumor Drug Tirapazamine

Fuqiang Ban,* James W. Gauld and Russell J. Boyd, Department of Chemistry, Dalhousie University, Halifax NS, Canada B3H 4J3

Tirapazamine and its metabolites are promising antitumor agents which can selectively kill the oxygen-poor cells in tumors. While it is known that tirapazamine derives its biological activity by causing DNA strand cleavage, the exact mechanism by which this occurs is not fully understood. The two N-O groups in tirapazamine (shown below) are recognized as the pharmacophores. At present, the attack of the N-oxide oxygen to a C1' sugar radical is proposed to be the major radical-mediated reaction by which tirapazamine cleaves DNA in tumor cells. However, several alternative mechanisms have also been proposed. We have employed density functional theory to investigate possible mechanisms by which tirapazamine may cleave DNA. Results obtained from these theoretical studies will be presented.

Roman Baranowski

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Poster: Collision-induced rotational alignment of NO$^+$ ions drifting in a helium buffer gas is studied with molecular dynamics using the {\em ab initio} potential surface of S.~K.~Pogrebnya~{\it et~al.} [Int. J.Mass Spectrom. Ion Proc. {\bf 149/150}, 207 (1995)], obtained via a coupled cluster singles-doubles approximation. We examine average translational and rotational temperatures, velocity and angular momentum distributions and the dependence of these quantities on the applied electric field. The distributions show that angular momentum is preferentially aligned perpendicular to the electric field vector. We investigate the mechanism of this alignment through a multi-polar moment expansion, and propose and demonstrate the accuracy of a bi-Maxwellian analytic form for describing the angular momentum distribution. We also investigate dependence of the angular momentum distribution function on the velocity distribution and compare the translational-rotational coupling with the recent experimental studies.

Andreas Becker

S-matrix analysis of laser induced ionization processes of molecules.

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We applied the so-called Intense-Field Many-Body S-matrix Theory to ionization processes of molecules in intense laser fields [1,2]. The approach is used to analyze the following features: The experimental observation [3,4] of suppressed molecular ionization of the oxygen molecule and its absence in the nitrogen molecule is found [5] to be due to a symmetry induced process dynamic effect.More generally, it is shown, that the class of homonuclear diatomic molecules that have active valence orbitals with anti-bonding symmetry would be suppressedbut not those with a bonding symmetry.The suppression effect can be visualized as due to an effective destructive interference effect between the two sub-waves of the ionizing electron emerging from the two atomic centers. Finally, the recently observed non-sequential double ionization of molecules is analyzed.

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NOTES

Nicholas V. Blinov

Quantum Molecular Dynamics studies of ultra-quantum helium systems

Nicholas V. Blinov and Pierre-Nicholas Roy, Department of chemistry, University of Alberta

In recent years, various experimental techniques have been developed to study chemical species solvated in helium nanodroplets. The extremely low temperature of the helium environment allows not only to isolate various solutes, but also to cool down their internal and translationnal degrees of freedom. From a theoretical standpoint, the equilibrium properties of helium clusters and solute particles can be described in the framework of the path integral formulation of statistical mechanics. This unique approach combined with Monte Carlo calculation techniques enables one to describe the equilibrium properties of many particles system from a microscopic point of view. Dynamical properties can be treated within the Centroid Molecular Dynamics (CMD) framework. Indeed, recent extensions of the CMD approach [Roy and Voth, J. Chem. Phys. 110, 3647 (1999)] make it possible to take into account particle exchange, essential to the description of the superfluid state of ultracold helium nanodroplet. In the present work, we apply the CMD approach to describe systems consisting of helium in the superfluid state. We also discuss the simulation of impurity particles embedded in helium nanodroplets.

Mary S.W. Chan

A Density Functional Study of Neutral Salicylaldiminato Ni(II) Complexes as Olefin Polymerization Catalysts.

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The recent discovery of the ability of salicylaldiminato Ni(II) complexes to promote ethylene polymerization opens the door to a new class of olefin polymerization catalysts. The major advantage of this type of catalysts is that they produce a neutral active center and thereby avoiding the ion-pairing problems encountered with the homogenous single-site catalysts in current use. The present DFT study investigates the polymerization mechanism followed by these neutral complexes as well as the electronic and steric effects of various substituents on the catalyst backbone. The addition of electron withdrawing or releasing substituents on the 5 position of the salicylaldiminato ring was found to result in small changes in the energetics of the reactions in the polymerization mechanism. This is most likely due to the substituent's remoteness from the active center. Changing the electronic nature of the atoms adjacent to the nickel results in larger shifts in energy. Finally, bulky substituents such as diisopropylphenyl and anthracenyl groups were found to have the largest effect on the reaction barriers and enthalpies in a direction that should substantially increase catalyst activity.

Stephan Chelkowski

Laser Control of Dissociative Ionization-Exact Non-BornOppenheimer Simulations for H2+

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Szczepan Chelkowski

“Laser Phase Directional Control of Photo-Fragments in H_2^+using Two-color, Intense Laser Pulses”

Szczepan Chelkowski, André D. Bandrauk, Laboratoire de Chimie Théorique, Université de Sherbrooke, Que. J1K 2R1, Canada.

Exact non-Born-Oppenheimer, numerical solutions of the time-dependent Schroedinger equation (TDSE) for the 1-D H_2^+ molecule in an intense, two-color laser field, have been obtained. Both, electron (ATI) and proton (ATD) kinetic energy spectra show spatial, correlated, asymmetric distributions. The calculated spectra exhibit the same unusual correlations as in experiments, in which both positively chargednuclear fragments and negatively charged photo-electrons were preferentially emitted in the same direction. The above asymmetries of photo-emission of electrons seen in our quantum simulation are interpreted in the framework of a quasi-static tunneling model and it is shown, that for the relative phase=0 the electron asymmetry is induced by the Coulomb attraction from the parent ion [1].

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“Measuring Dissociating Wave Packets by Laser Coulomb Explosion Imaging”

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From exact non-Born-Oppenheimer simulations of dynamics of H2 in an intense , $I > 10^{15}$ W/cm^2 ultrashort laser pulse ($t_p < 5$ femtoseconds), we show that it is possible to measure the time evolution of the probability distribution $|\psi(R,t)|^2$ of a dissociating wave packet. In our simulation, a pump-probe technique is used: first, a weaker laser photo-dissociates the molecule, and next ,with experimentally controlled time-delay t_0, a second, intense ($I > 10^{15}$ W/cm^2), ultrashort laser is applied. The latter, ionizes “instantaneously” the dissociating molecule. Measurement of the kinetic energy spectra of exploding fragments allows us, with the help of the inversion based on Coulomb’s law and classical conservation of energy, to reconstruct the shape of the probability distribution $|\psi(R,t)|^2$ at time $t=t_0$. By repeating this experiment for many time delays t_0, we can obtain a detailed information about the time evolution of the system. The theory of Coulomb explosion imaging of moving wave packets and limitations of the above classical inversion method are presented [1].

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Shafinaz Chowdhury

Structure Based Design Of Protozoal Dihydrofolate Reductase Inhibitors

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This work concerns the design, synthesis, and evaluation of inhibitors of leishmanial and trypanosomal dihydrofolate reductase. Initially study was made of the structures of the leishmanial and human enzyme active sites to see if there were significant differences which could be exploited for selective drug design. Then a series of compounds were synthesized based on 5-benzyl-2,4-diaminopyrimidines. These compounds were assayed against the protozoan and human enzymes and showed selectivity for the protozoan enzymes. The structural data was then used to rationalize the enzyme assay data. Compounds were also tested against the clinically relevant forms of the intact parasite. Activity was seen against the trypanosomes for a number of compounds. The compounds were in general less active against Leishmania. This latter result may be due to uptake problems. Two of the compounds also showed some in vivo activity in a model of African trypanosomiasis.

Steve Chrétien

Density functional study of the adsorption of small hydrocarbons on iron clusters, Fen/Fen+ (n=1-4).

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An extensive study of the adsorption of C2H2, CCH2, n-C4H4, c-C4H4 and C6H6 on iron clusters is presented. Binding energies and equilibrium structures for the various ligands are discussed. This study constitutes a good starting point for the understanding of the formation of benzene, from acetylene, on iron clusters. A detailed study of benzene formation on Fe and Fe+ is in progress. Preliminary results explain why no C4H4 unit are observed experimentally [1] although it seems to be an important reaction intermediate in the cyclotrimerization of acetylene on Pd(111) surface[2] and on U+[3].

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Phillip A. Christiansen

Ab Initio Quantum Capping Potentials for QM/MM Calculations.

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We show that conventional ab initio methods for generating effective core potentials can also be used to form one-electron carbon potentials for capping quantum regions in hybrid QM/MM calculations. To incorporate capping potentials into common electronic structure codes will require the addition of a nucleus-nucleus shielding function, a normal byproduct of the conventional potential generating process.

Qizhi Cui

Analysis of Solvation Structure and Thermodynamics of Alkanes in Water by Reference Interaction Site Model Theory Using All-atom Model

Qizhi Cui and Vedene H. Smith, Jr., Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

All-atom molecular model and optimized site-site pair potential parameters are employed for alkane solutes. By reference interaction site model theory, methane and ethane hydration structures are analyzed at the atomic level and their hydration free energy, energy and entropy are calculated. Our calculated thermodynamic properties are in rather good agreement with experiments.

Laurent David

Parametrization of the lead ion, application to the leadzyme

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The Lead(II) ion is an important metal ion for the leadzyme, a small ribonucleic acid enzyme (ribozyme). Molecular mechanics simulations on bioorganic molecules containing inorganic compounds, such as metal ions, are usually performed using non-bonded interactions. More accurate simulations of these mixed systems require metal ion coordination factors and, thus, we parameterized Lead(II) using bonds and bond angles. The structures containing Lead(II) ions in the Cambridge Structural Database were used to estimate, using potential of mean force, the different force constants, and the equilibrium distances and angles. The parameters were determined for the existing force fields, and for the new developed potential energy terms. By selecting a small subset of structures containing Lead(II), the computed parameters were optimized using a Simulated Annealing-Downhill Simplex Method. The new developed parameters were finally applied to energy-minimized the leadzyme-Lead(II) complex.

Eugen Deretey

Theoretical Study of Excited States of Planar Structures of 1, 3-Dimethylallene

Eugen Deretey (1), Paul Brumer 1) and Moshe Shapiro (2)

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(2) Chemical Physics Department, The Weizmann Institute of Science, Rehovot, Israel

Ab initio molecular orbital computations employing configuration interaction singles (CIS), complete active space self-consistent field (CASSCF(4,6)) and hybrid density functional theory using the B3LYP methods were applied to study the geometries of the excited state planar 1,3-dimethylallene structure. The Potential Energy Surfaces (PES) for the first three electronic excited states were determined through rigid scan, spanning the bending modes of C=C=C and the dihedral angle between the two planes defined by carbon atoms from the H3C-C=C and C=C-CH3 groups. Next, several critical points located on the first excited state PES, involving the in-plane-bending, were optimized. For 1,3-dimethylallene we studied the linear and bent geometries with anti and syn methyl orientations. For each species the open shell and closed shell singlet electronic configurations were taken into consideration. The results of the computation show that the excited state structures are of closed electronic shell.

Adam Dickie

"Theoretical Studies of Self-Assembled Tin-Alkynyl Thin Films on Inorganic Oxide Surfaces"

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Acid-base hydrolysis of aminostannanes with dialkyne terminated chromophores, containing either alkyl or aromatic type backbones, has been used to construct thin films on Si(100)/SiO2 substrates. Molecular mechanic calculations on hexagonal models of Sn-(CC)m-R-(CC)m-H (R = -(CH2)n-, -C6H4- ; n = 2-10, m = 0-2) are used to interpret the intermolecular forces of self-assembly. Evaluating the non-bonded interaction energy of the chromophores at different molecular twists (z-axis rotation), in-plane tilts (y-axis rotation), and out-of-plane tilts (x-axis rotation) gives the lowest energy packing structures over an intermolecular separation range of 4.0-5.0 Å. The intermolecular alkyl or aromatic backbone forces dominate the self-assembly in these thin films. The close-packing of alkyl chains allow a favourable molecular fit between the terminal dialkyne groups; with aromatic backbones, such a fit is not possible because of the large phenyl cross-sectional area. Experimental applications of the chromophore thin films, such as multilayer formation, polymerization, and Co(CO)8 adsorption, are also interpreted from the packing calculations.

Gino A. DiLabio

Density-Functional Theory Studies of Uric Acid, Vitamin C, and Vitamin E.

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Recently developed DFT-based model approaches have been shown to predict X-H bond dissociation enthalpies (BDE's) to within 1-2 kcal/mol [1]. These techniques have been applied, with solvation models, to uric acid and vitamins C and E in order to study the activity and behaviour of these common biological antioxidants.

The urate anion is found to have a BDE of 73.8 kcal/mol compared to a calculated BDE of 74.8 kcal/mol for vitamin E. However, the inclusion of solvent effects indicates that the reaction between urate and the vitamin E radical is endergonic by about 2.3 kcal/mol. The reaction between the ascorbate anion and vitamin E is computed to be exergonic by 7.7 kcal/mol, indicating that vitamin C readily regenerates vitamin E. These results are in agreement with experimental findings [2]. The reduction of ascorbate results in the formation of ascorbyl free radical (AFR). AFR readily undergoes disproportionation to generate ascorbate and dehydroascorbic acid (DHA). Our results show that the disproportionation of AFR is driven structural changes (hemiketal formation) in the DHA molecule [3].

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NOTES

Piotr Drabik

The investigation of the effects of counterions in protein dynamics simulations.

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Molecular simulations able to exactly represent solvated charged proteins are helpful in understanding protein dynamics structure and function. In the present study we have used two different starting structures of papain (a typical, stable, globular protein of intermediate net charge) and different modeling procedures to evaluate some effects of counterions in simulations. A number of configurations have been generated and relaxed for each system by various combinations of constrained simulated annealing and molecular dynamics procedures, using the AMBER force field. The analysis of trajectories shows that the protein sensitivity to the presence of counterions is highly dependent on the starting model and different procedures of equilibration used. The neutralized systems tend to evince smaller root mean square deviations regardless of the system investigated and the simulation procedure used. The results of parameterized fitting of the simulated structures to the crystallographic data, giving quantitative measure of the total charge influence on the stability of various elements of the secondary structure, revealed a clear scatter of different reactions of various systems' secondary structures to counterions addition: some systems apparently were stabilized when neutralized, while the others were not. Thus, one cannot unequivocally state whether protein secondary structures are more stable when they have neutralized charges, which suggests that caution should be taken when claiming the stabilizing effect of counterions.

Toshikazu Ebisuzaki

First-principles study of the ethylene-Pd(110) adsorption system

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The hydrogenation of ethylene promoted by transition metal catalysts represents an important process for the industrial production of ethane. Although this process has been the subject of several experimental investigations, the first one carried out in 1934 by Horiuti and Polany [1], several of its aspects are still a matter of intense study. For example, the adsorption mode of ethylene strongly depends on the nature of the metal surface, temperature and coverage conditions. Surface science techniques [2] as well as density functional theory calculations [3] have been succesfully employed in order to investigate the nature of the surface-adsorbate interaction. The latter, in particular, have been fostered by the advent of newly discovered algorithms, such as the Car-Parrinello method [4], which combines density functional theory (DFT) with molecular dynamics (MD) simulation.

In this poster we will present the results of our first-principles DFT calculations on the structure and energetics of the ethylene-Pd(110) adsorption system. The calculations revealed that, when the ethylene molecule is π-bonded on Pd(110), tilted configurations are preferred over those with the C=C molecular axis parallel to the metal surface. Furthermore, the adsorption states on clean Pd(110) surface will be compared with those on the hydrogen-coadsorbed Pd(110) surface. The latter are important to the study of ethylene hydrogenation on transition metal surfaces.

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Howard Feldman

A Rapid, Probabilistic Protein Conformer Generator

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We have developed a method to generate all-atom protein conformers of arbitrary amino acid composition in O(NlogN) time, taking only the primary sequence as input and building approximately 1 structure/s. These conformers possess physically and chirally valid backbones with all bond lengths, angles and dihedrals within the allowable tolerances. In the method, new Ca positions are chosen according to a 2-D probability distribution function called a “trajectory distribution” seeded by sampling a non-redundant set of protein structures, which biases the sampling at each residue, and the remaining atoms are placed to minimize the error in the various bond lengths and angles these atoms determine. When van der Waals collisions occur between atoms, the algorithm backtracks. Sidechain rotamers are chosen using probabilistic sampling of Dunbrack et al’s backbone dependent rotamer library. Generated random proteins behave as Flory polymers. By convolving a 3-state secondary structure prediction with separate trajectory distributions for helix, sheet and coil at each residue, the walk can be biased by the prediction producing more correct secondary structure. In a pool of 500,000 conformers of a small peptide, 1VII, the closest structure to the native state was found to have 3.1A RMSD. The random conformer generator may be used to generate starting points for molecular dynamics simulations, ensembles of a protein for comparison with experimental studies of disordered structures and the exploration of the conformational space involved in domain packing in large multidomain protein structures.

Alexandre Foisy

Numerical Calculations of Ionization Rates in Molecules via Time-Dependent Schroedinger
Shroedinger equations and tunneling models at high laser intensities.

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It has been shown in the past few years that short intense laser pulses can provide the extremely fast ionization of small molecules ans ions like H_2^+. High performance computing is a relatively fast and efficient way to study this phenomenon. In this presentation, we will show the range of wavelengths and intensities that have been studied, as well as the advantages and disadvantages of high performance computing, with emphasis on the differences between 1-dimensional and 3-dimensional calculus.

Tammy L. Gosse

Stereoselectivity in the Diels-Alder Reactions of 1,3-Butadiene with 3-Substituted Cyclopropenes

James D. Xidos, Tammy L. Gosse, Diane Burke, Raymond A. Poirier, and D. Jean Bumell

The facial and endo/exo selectivities in the Diels-Alder reactions of 1,3-butadiene with a variety of 3-substituted cyclopropenes are investigated at the HF/6-31++Gr* level. Of the four modes of addition, it is predicted that endo-and addition is favored in most cases, followed by exo-anti addition. Anti addition is always predicted to be preferred over syn addition for this reaction. Results suggest that the primary factor that determines endo-anti vs exo-anti selectivity is the difference in the energy of interaction between the two addends in the transition state. This difference may be due to secondary orbital interactions between the diene and cyclopropene in the endo transition state. Except for SiH3, all of the substituents examined stabilize the cyclopropene ring in the ground state, and most substituents are more destabilizing than H in the transition state. For endo-anti addition, the transition state is significantly destabilized by an electronegative substituent and stabilized by an electropositive one. An examination of HOMO energies and geometry changes in the transition state suggests an inverse-electron-demand mechanism for this reaction.

Peter Guthrie

Predicting the Rates of Reactions in Solution Using Distortion Energies (from MO calculations) and Experimental Equilibrium Constants

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No Barrier Theory asserts that when only one thing happens in a chemical reaction there is no kinetic barrier, but only a quadratic potential function, and that the kinetic barriers associated with almost all chemical reactions result from the need for more than one simple thing to happen simultaneously for the reaction to occur. This theory permits calculation of the free energies of activation for chemical reactions given only the equilibrium constants in solution and the distortion energies corresponding to the hypothetical “one thing at a time” transformations. The method is quite general and in principle provides a way to calculate the rate of any chemical reaction, for which the equilibrium constant is known, with no adjustable parameters and relatively modest computational requirements. This approach will be illustrated for heterolytic, homolytic, and pericyclic reactions, including imine formation, free radical addition to alkenes, and the ring opening of cyclobutene to butadiene.

Frank Hagelberg

Quasi-spherical Structures of Copper-doped Silicon Clusters (CuSin, n<13).

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The chemistry and physics of metal-doped silicon clusters have stimulated much recent research activity, which can be attributed to the fact that these units are the microscopic counterparts of materials with the very highest relevance to modern electronic devices.

However, the systematics of metal-silicon clusters can claim considerable interest on its own. Thus, it has turned out that an Si(n) framework may be stabilized in a fullerene-like geometry through the presence of an endohedral metal impurity. This effect is investigated here for the case of CuSi(n) clusters which have been experimentally observed by means of mass-spectrometry /1/. Through computational analysis employing Density Functional Theory, we find a strong preference of exohedral Cu sites for the smaller of the units explored, i.e. CuSi(n) with n < 10. A quasi-spherical, geodetic shape with a central Cu impurity, however, is identified for the CuSi10 cluster. This finding offers an explanation for the experimentally established predominating abundance of the CuSi10 unit.
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Sébastien Hamel

Towards an implementation of RI-OEP in TDDFT

An accurate computation of excited states and orbital energies is important for the design of new materials for photonic and nanoelectronic components.

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Time-dependent density functional theory (TDDFT) is a relatively simple yet, in principle, rigorous method for treating electronic excited states. This makes it a choice candidate for exploring excited state potential energy surfaces for applications in photophysics and photochemistry. For a good description of higher excitation energies with TDDFT, an accurate treatment of the asymptotic region, where the usual LDA and GGA functionals behave poorly, of the exchange-correlation potential is critical. More and more this leads to the use of some variant of the optimized effective potential (OEP) method in TDDFT. The OEP method gives the exact Kohn-Sham exchange potential (up to a certain linear response approximation) and thereby corrects the behavior of the exchange-correlation potential. However the computational difficulty of OEP-type calculations grows nominally as ${\cal O}(N^4)$ with the size of the system and becomes prohibitive for large systems and so one would like to use the resolution-of-the-identity (RI) auxiliary-function approach, an approximation used to eliminate the need to calculate 4-center integrals, albeit with some loss of accuracy.

Roothaan-Hartree-Fock (HF) has been implemented in {\sf deMon-DynaRho} within the RI approximation as a first-step towards RI-OEP. The accuracy of this RI-HF method has been tested for the total energies and orbital energies for several small molecules (CO, N$_2$, CH$_2$O,C$_2$H$_4$) frequently used to test new methods for calculating molecular excitation spectra, to examine the level of confidence one can have in orbital energies from RI-HF as this may limit the accuracy we can ultimately hope for in our RI-OEP orbital energies.

Tina Hayward

Equations of State and Phase Coexistence Properties for Water Potentials

Tina M. Hayward, Alexander Yu. Zassetsky and Igor M. Svishchev, Department of Chemistry, Trent University, Peterborough, Ontario K9J 7B8

Computational techniques provide a detailed understanding on the molecular level of the thermodynamic properties, dynamics and structure of fluids. At present, considerable efforts are devoted to the development of refined water models for computer simulations that explicitly incorporate molecular polarizability. A major incentive for this advancement is a practical need to examine both ambient and low-density (high-temperature) water near and above the critical point with a single transferable potential. Thermodynamic properties for two water models are presented in this contribution based on a series of extensive molecular dynamics simulations. Accurate analytical equations of state for the simple point charge (SPC/E) and the polarizable point charge (PPC) water potentials are given for a wide range of state conditions. Their liquid-vapor coexistence properties and the critical point parameters are compared to those of other models for water and experimental data. The effect of applying an external electric field to the system on the coexistence properties is investigated. A shift of the critical point of water to higher temperature and pressure is observed a result similar to that of the introduction of an electrolyte to water.

Zhenming Hu

Electronic Structures and Reactivities of d8 transition metal dicarbonyl complexes: Comparative ab initio theoretical studies.

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Hiroshi Nakatsuji, Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

An exciting development in catalytic chemistry in recent years has been the use of transition-metal complexes and surface species to activate the normally unreactive C-H bonds in alkanes and Si-H bonds in siliconalkanes. In this regard there is a renewed interest in the electronic structure, catalytic reactivity and photochemistry of (C5H5)M(CO)2 (M=Rh, Ir), [Cl2Rh(CO)2]- and Rh(CO)2/Al2O3 systems and the reaction mechanism towards the oxidative addition of typical organic molecules. The present presentation will focus on two related aspects.

First, we report a comparative theoretical study of the equilibrium geometries, vibrational frequencies and the reaction energetics of the Rh-CO bond activation of the [Cl2Rh(CO)2]- and [Cl2RhCO]- complexes. The B3LYP density functional and the traditional correlated MP2, QCISD and CCSD(T) methods are used to give a comprehensive assessment of ab initio methods for the study of transition metal complexes. Second, the electronic structures and the catalytic activities of (C5H5)M(CO)2 (M=Rh, Ir) and [Cl2Rh(CO)2]- will be discussed. These studies present a deep fundamental understanding of the nature of the catalytic activity of d8 transition metal dicarbonyl complexes. Future research will be designed to clarify the photochemistry of the d8 transition metal dicarbonyl complexes and surface species.

Thomas Huber

Molecular Dynamics Simulations on Purpose Specific Computer Hardware

Thomas Huber and Alistair Rendell, Australia. National University Supercomputer Facility, The Australian National University, Canberra, ACT 0200, Australia

For many years particle dynamics calculations have been a popular tool used to investigate dynamic behaviour of complex N-body systems. One class of dynamics simulation is molecular dynamics in which dynamic molecular behaviour is simulated based on equations of motion from classical mechanics. To simulate the dynamics of a molecule by numerical, integration of Newton’s equations of motion the time step is required to be small enough to resolve the

highest frequency mode in the system. In a molecular system this is typically bond stretching motion and a time step of 1 fs (10-15s) or less is required. However, the time scale on which most biologically interesting processes take place is in the microsecond range and 10' integration steps are necessary to simulate such a process. For a typical biomolecular system a single integration step takes between 1 and 10 seconds on todays high end workstation.- A researcher is either forced to be very patient or needs access to much more expensive supercomputers.
To overcome this limitation we investigate the use of high performance, purpose specific computer hardware to perform the most time consuming tasks in an MD simulation. This approach seems to be highly promising considering the inordinate success of (cooperative) special purpose hardware (e.g. mathematical co-processors and graphics acceleration cards) in other areas of computing. Our work is a collaboration with Prof. Ebisuzaki and his group at The Institute of Physical and Chemical Research (RIKEN) in Tokyo, which has many years of expertise in the design of purpose specific hardware. Currently the group is in the final stages of testing the 2nd generation hardware (called GRAPE and WINE). This is used to calculate pairwise interactions between N bodies and of any functional form. The peak performance of the 2"d generation chip is estimated to be 16.4 Gflops. To give a comparative scale, this is nearly twice as fast than the peak performance of the fasted currently available general purpose processor, the Fujitsu VPP5000 vector processor.

We will present simulation results obtained with GRAPE/WINE hardware and compare them with simulations performed on conventional computer platforms.

Derek Hunter

Dynamics of Diffusion in Mesoscopic Argon Clusters

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Studies of diffusion in liquid argon clusters in the mesoscopic regime are presented. Simulations were performed using Molecular Dynamics techniques. The diffusion coefficients and activation energy barriers for the diffusion process are computed using Lennard-Jones versus more accurate interatomic potentials. The diffusion mechanisms show unique features in comparison to bulk analogues.

Margaret M. Hurley

Gun Tube Erosion from a Theoretical Perspective M.M. Hurley, C.F. Chabalowski, Dan Sorescu, and G.H. Lushington

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Iron surfaces and their interactions with small gaseous molecules such as CO play a vital role in a wide range of processes, of interst to both the military and industrial communities. One example is the wear and erosion of gun tube surfaces by carburization, oxidation, hydrogen embrittlement, and similar processes. We use both pseudopotential planewave (CASTEP, VASP) and FLAPW (WIEN) codes to study the interactions of CO and O2 on the (111) and (100) surfaces of BCC iron as an initial step in understanding gun tube erosion. We are also interested in performing molecular dynamics simulations on the model system.

Toshiaki Iitaka

Order-N calculation of response functions

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As first-principles calculations become more and more important in various research fields such as physics, chemistry, materials science, and recently geology and biology, the demand for calculation of larger and larger systems is growing rapidly.

One of the answers to this demand is the so-called order-N methods, which compute the electronic band structure, the total energy, and other quantities with computational time and storage proportional to N, the number of the atoms in the system.

For very large systems, these methods are much faster than the conventional diagonalization methods, which require computational efforts proportional to N^3. % density-matrix

The order-N methods may be classified into two steps. The first step is minimizing the total energy to obtain the ground state of the self-consistent one-particle Hamiltonian. The second step is extracting dynamic properties such as linear and nonlinear-response functions from this Hamiltonian.

While the first step has been extensively studied and also comprehensive reviews are available, the second step has been studied by only few papers, including the {\it particle source method} (physics/9802021) and the {\it projection method} (PRE vol.56, p.1222), which use the numerical solution of the time-dependent Schr\”{o}dinger equation, and {\it projected random vectors}.

The purpose of this presentation is to review the recent development of the projection method and to extend its formalism to nonorthonormal basis sets (PRE vol.61 p.R3314), on which many order-N total energy minimization methods are built, so that the full {\it ab initio} calculation from the total energy minimization to the response function is possible.

Sehiro Iwata

Theoretical photoabsorption spectra of metal-water clusters and water cluster anions

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Recently we found a unique structural unit, OH{e}HO in the group 1 metal - water clusters. The calculated harmonic frequencies of HO stretching modes suggest that the interaction between HO and the electron cloud {e} is as strong as the ordinal hydrogen bonds; thus we may call it “electron hydrogen bond”. In the present work, we theoretically study the photoabsorption cross section of the system to characterize the nature of the bond more clearly.

NOTES

David Jack

An order-disorder transition in monolayer N2 on NaCl(001)

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The results of Monte Carlo simulations are presented which predict that a monolayer of N_2 adsorbed on the the NaCl(001) surface will adopt an ordered p(2x1) structure at temperatures below T=25 K. The nitrogen molecules are tilted by 29° from the surface normal and form azimuthally ordered rows which alternate their orientation from row to row. Above 25 K the molecules become azimuthally disordered but with residual short range order in the form of pairs of counter rotating vortices. This transition exhibits Ising-like behaviour in the form of a logarithmically divergent heat capacity. However, the critical exponents for the order parameter and susceptibility have nonuniversal values which nonetheless satisfy the Rushbrooke scaling law $\alpha + 2\beta + \gamma = 2$.

Araz Jakalian

Fast, Efficient Generation of High-Quality Atomic Charges: AM1-BCC Model

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The AM1-BCC method quickly and efficiently generates high-quality atomic charges for use in condensed phase simulations. Underlying electronic structure features including formal charge and delocalization are first captured by AM1 atomic charges. Bond charges corrections (BCCs) are then added using a formalism identical to the consensus BCI (bond charge increment) approach. These BCCs have been parameterized so as to reproduce the HF/6-31G* electrostatic potential of a training set of >2700 compounds. The training set samples most organic functional groups and their combinations, as well as a wide variety of cyclic and fused bicyclic heteroaryl systems. The resulting BCC parameters allow the AM1-BCC charging scheme to handle virtually any compound in the Merck Index and the NCI Database of small molecules. Dimer calculations and relative free energies of solvation of a diverse test set of compounds demonstrate that the performance of these charges is comparable to that of HF/6-31G* RESP charges. We therefore propose this model for general use to generate charges for biologically and pharmaceutically relevant small molecules for condensed phase simulations.

Isao Kawata

Analyses of the mechanism of the Coulomb explosion of H2+ subjected to intense femtosecond laser pulses.

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We investigate the mechanism of the coulomb explosion of H_2^+ in strong femtosecond pulses. In order to analyze Coulomb explosion in real-time the time-dependent Schroedinger equation for the 3D model Hamiltonian of H_2^+ is solved numerically by using our developed dual transformation method. In the 3D model, the nuclear motion is restricted to the polarization direction of the laser electric field and the electron is allowed to move in three dimensions. The doorway state for ionization is revealed by projecting the wave packet onto the

phase-adiabatic states which are defined as time-dependent eigenfunctions. It is found that the two phase-adiabatic states |1> and |2> are the key states for the dynamics and ionization proceeds via |2>. This shows that |2> is the doorway state of ionization. The 3D packet calculated in the 3D model is mapped onto the two states and we obtain the nuclear distributions on these states. From the distribution on |2>, we can evaluate the kinetic energies of the dissociative fragments of Coulomb explosion by estimating the critical internuclear distance and the critical momentum when ionization proceeds. Thus, our methodology enable us to do the real-time analyses of various molecular processes in intense laser fields.

Philip Kiefer

A New Theory for Kinetic Isotope Effects for Proton Transfer in a Polar Environment

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A nontraditional theory for primary isotope effects for proton transfer reactions is presented. In this view, the reaction coordinate for proton transfer is related to the environmental reorganization rather than the coordinate of the proton itself. The theory describes primary isotope effects for both (i) adiabatic proton transfer, in which the proton motion at the transition state in an environmental (e.g. solvent) coordinate is vibrationally above the barrier in the proton coordinate, and (ii) nonadiabatic proton transfer, in which the proton tunnels through the barrier in the proton coordinate. It is shown that this description leads to H/D kinetic isotope effect (KIE) predictions, such as the behavior of the KIE with reaction asymmetry, that have long been thought to support the traditional view of proton transfer. The important role of the proton donor- proton acceptor vibration in proton transfer (PT) reactions and its impact on KIEs will also be discussed.

Stephen T. Kim

QSAR aromatic beta-substituted novel compounds for biological activity

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QSAR (Quantitative structure activity relationship) was done on 41 aromatic substituted beta-amino acids for biological activity. Using principle component analysis and multiple linear regression 11 descriptors were found to predict biological activity with a correlation coefficient of 0.83. Furthermore, a representative molecule's structure was solved using X-ray crystallography and the density wavefunction was calculated using a 631G*/B3LYP optimized structure. The results show unique regions of negative electrostatic potential that may be important for receptor binding.

Nadya Kobko

The Role Of Counterpoise Correction For BSSE In The Geometry Optimization Of The Transition States

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A method and a code for gradient geometric optimization of molecular complexes on counterpoise corrected (CP) potential surfaces was developed recently by S. Simon, M. Duran, J. J. Dannenberg and P. Salvador. It was shown that geometric optimization on CP-corrected potential energy surfaces improves the description of different systems by the ab initio and DFT methods and may help to eliminate or reduce some artificial effects due to incomplete basis sets. For instance, intermolecular separation increases for H-bonded dimers upon CP corrected optimization. In the present work the method was used to perform a theoretical study of the four different chemical reactions: (1) Diels-Alder reaction of ethylene and butadiene via symmetric transition state; (2) the 1,2-shift of proton in ethyl radical; (3) hydrogen transfer between methyl radical and methane, (4) hydrogen transfer between methyl radical and propene. To our knowledge, CP corrected optimization was applied to the transition states (TS) for the first time.

For the Diels-Alder reaction between ethylene and butadiene the reaction coordinate at the TS is primarily the approach of the two fragments toward each other. We found that the CP-optimization increases the intermolecular distance in the TS. In the case of the H-shift in ethyl radical the system appears to have a transition state with the H-atom symmetrically placed with respect to the two carbons. We found it to be an artifact of the calculations up to HF/6-311++G** level. The CP-optimization also removes multiple local minima on DFT potential surface. The system in the third case has a symmetric transition state and the reaction coordinate is primarily involves motion of the H-atom between the two carbon atoms. The CP correction increases the distance between the carbons in TS. In the last case the system is unsymmetric and CP correction elongates the distance between the H-atom and the methyl radical slightly less than the distance between H and allyl radical in the transition state.

Denise Koch, Gilles H. Peslherbe, Holger Vach

Translational and Rotational Product Energy Distributions of (N2)n Cluster Surface Scattering.

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When molecular or atomic clusters are scattered on a solid surface at supersonic velocities, extreme pressures and temperatures are produced within the cluster which can lead to chemical reactions. Elucidating the mechanisms and dynamics of energy transfer upon surface impact is a key step in understanding these surface-catalyzed reactions. In a recent experimental study, De Martino et al. (J. Chem. Phys. 1999, 111, 7038) measured the translational and rotational state distributions of the monomer products of (N2)n cluster scattering on a graphite surface. It was found that the translational states follow a single Maxwell-Boltzmann distribution whereas the rotational state distributions are represented by a sum of two distinct Boltzmann distributions. A satisfactory explanation for these differing behaviors could not be inferred from the experimental results. We investigate by means of molecular dynamics simulations the dynamics of surface-induced (N2)n cluster fragmentation.Analysis of the scattering dynamics provide a molecular-level explanation for the differing behaviors of energy transfer to the translational and rotational modes of the monomer products.

Dr. Pierre Lavigne

Structure-based thermodynamics in the analysis of docked protein-ligand complexes : Towards a more realistic scoring function

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We used a structure-based thermodynamic (SBT) approach to calculate the enthalpy (DH°d), entropy (DS°d), heat capacity (DCp) and Gibbs free energy (DG°d) of dissociation of docked complexes between microcystin-LR (MLR) and the catalytic domain of protein phosphatase-1 (PP-1c). We show that the lower the r.m.s.d. of the complex (compared to the X-ray structure), the closer the corresponding DG°d is to the target one (DG°d of the X-ray structure of the complex). We also note a significant scatter in r.m.s.d. within the complexes of highest affinity; a situation reminiscent of the 'docking problem'. On the other hand, the corresponding DH°d and DS°d show a compensation effect with a compensation temperature (Tc) similar in magnitude to experimental values reported. As demonstrated, the SBT approach allows for the simulation of structural fluctuations in protein complexes and cooperativity of ligand binding in solution. We discuss the use of SBT to account for conformational fluctuations in the scoring of docked complexes

Francois Legare

Laser Control of Excitation and Alignment of Molecules by CARP-Chirped Adiabatic Raman Passage via Time-Dependent Schreodinger Calculations

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François Légaré

Preparation and Alignment of Highly Vibrationally Excited Molecules by CARP -Chirped Adiabatic Raman Passage

F. Légaré, S. Chelkowski, A.D. Bandrauk, Laboratoire de Chimie Théorique, Faculté des Sciences, Université de Sherbrooke, PQ, Canada J1K 2R1

3-D time-dependent Schrödinger equation simulations of Raman excitation of the Cl_2 molecule are used to demonstrate the feasability of efficient high vibrational excitation ($v > 20$) of symmetric nonpolar bonds using short (ps) chirped frequency laser pulses at intensities below the ionization treshold ($I = 2x10^{13}$ W/cm^2). The process, called CARP, Chirped Adiabatic Raman Passage, involves sequential Raman excitations $\Delta v = +1$ during the pulse accompanied by rotationnal transitions. It is shown that as a result of CARP, considerable laser alignment of the molecule is achieved in high vibrational levels, thus offering a new tool for the study of dynamic and reactivity of aligned excited molecules.

Jolanta B. Logowski

Ab Initio Investigation of Excitation Energies of Thiophene, Cyclopentadiene and Fulvene based π-Conjugated Polymers

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Using the configuration interaction (singles, CIS), an ab initio theoretical approach that includes some correlation effects, we investigated the nature of the geometric conformations and electronic transitions in in pi-conjugated oligo(thiophene)s, oligo(cyclopentadiene)s, oligo(fulvene)s and their cyano based derivatives. Geometry optimizations were first carried out with the Hartree-Fock method; starting from the resulting HF geometries, the excitation energies were determined using CIS method. In agreement with several previous theoretical/experimental studies, this investigation provides evidence that the cyano substituted molecules have considerably smaller intrinsic band gaps than their parent molecules. The results of CIS/3-21 G* oligomer calculations also show that delocalized excited states are accompanied by a strong geometric deformation in comparison to their ground state geometries. The inclusion of electron correlation. results in a significant reduction in band gaps (in comparison to Hartree-Fock values) and shows excellent agreement with the experimental band gap values (~0.1-0.5 eV).

Chris Lovallo

Structure and Spectra of Group IVA Tetrahalides

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The Group IVA tetrahalides MX4 (M=Ti,Zr,Hf;X=F,Cl,Br,I) were studied using Model Core Potentials to replace the core electrons of all the atoms. Structures as well as the infrared and ultraviolet photoelectron spectra have been calculated at both the Hartree-Fock and correlated (MP2, DFT) levels of theory. Comparisons between the various methods and experimental results will be discussed.

H.Z. Lu

New Numerical Method With Moving Grid for Time-Dependent Schroedinger Equations of Molecules in Intense Laser Pulses

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We write the time-dependent Schroedinger equation (TDSE) of molecules in intense laser field in the velocity gauge and we use a Lagrangean moving system. The discretization of the obtained equation by a finite difference/ADI method result in a simplified discrete system on a moving grid and permits the best approximation of the classical laser-molecules interaction. |To improve furthermore the efficiency of the method, we have adopted a non-uniform, adaptive grid to concentrate the grid points in the region of interest. This new numerical integration method has been used to calculate exactly the ionization of H_2^+ ion in a short intense laser pulse which is parallel to the internuclear axis or circular, perpendicular to the internuclear axis with eventually the presence of a magnetic field parallel to the internulcear axis. The efficiency of our new method has been proved by comparing the convergence of the calculated ionization rate in function of the fixed internuclear distance with other usually used method.

Arthur Michalak

Ab Initio Molecular Dynamic Simulations Along The Intrinsic Reaction Path

Arthur Michalak and Tom Ziegler, Department of Chemistry, University of Calgary, 2500 University Drive, Calgary, Alberta, Canada T2N 1N4.

A choice of a reaction coordinate in the slow growth molecular dynamics is important for obtaining correct estimates of the reaction free energy barriers. We present results of the slow growth simulations [gradient corrected DFT with the projector-augmented wave (PAW) method], in which the molecular system is dragged from the transition state toreactants/products along the intrinsic reaction path (IRP). In our approach, the IRP is first determined by the steepest descent in the mass-weighted cartesian space starting from the transition state, then the finite-temperature simulation is performed with the linear constraint which fixes the projection of the atomic positions vector on the IRP at every time-step. The free energy change is obtained by integrating the force on constraint along the IRP. We present the results for the HCN —> CNH and the CH_2=CH-CH_2Cl —> ClCH_2-CH=CH_2 isomerization reactions, the prototype SN_2 reaction Cl- + CH_3Cl —> ClCH_3 + Cl^-, the conrotatory ring opening of cyclobutene, and the olefin capture in the ethylene polymerization catalyzed by Brookhart Pd(II) diimine-complex.

Arthur Michalak

Theoretical Studies On Polymerization And Co-polymerization Processes Catalyzed By Late Transition Metal Complexes

Arthur Michalak and Tom Ziegler, Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

We present the results of theoretical studies on the polymerization and co-polymerization reactions of ethene, α-olefins, and acrylates catalyzed by late transition metal complexes. The substituent effects on the factors controling polymer branching, such as relative stabilities of isomeric alkyl and olefin complexes, as well as the regioselectivity of olefin insertion have been studied by gradient corrected DFT calculations for N^N-Pd(II) complexes, with N^N = -NAr-CR-CR-NAr-, Ar = -C6H5, -C6H3(Me)2, -C6H3(i-Pr)2, and R = H, -CH3, C10H6. Further, the growth and isomerisations of polymer chain have been modeled by stochastic approach.. The co-polymerization of α-olefin with acrylates have been studied by DFT calculations for Pd(II) and Ni(II) complexes with Brookhart's and Grubbs' ligands; relative insertion rates and stabilities of intermediates have been determined and compared with the available experimental data. The acrylate binding mode have been compared for a variety of transition-metal based olefin polymerization catalysts, in order to identify those potentially able to catalyze α-olefin co-polymerization with polar group containig monomers.

Tzonka Mineva

Orbital Fukui indices and regional softness from perturbed Kohn-Sham orbitals and Mayer atomic charges

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Three alternative approaches for computing the chemical reactivity descriptors are derived in the framework of density functional theory. The proposed schemes consider the computation of orbital Fukui indices, where all valence orbital are taken into account; the Fukui indices of each atom in the molecules from atomic hardness values, called here atomic Fukui indices; the regional Fukui indices obtained from the regional softness, expressed in mixed LCAO representation of second quantization as functions of Mayer bond-order indices and Mayer atomic charge. Before going to the Fukui values, the hardness matrix is construct from the Kohn-Sham orbitals by the use of fractional occupation number concept and Janak's extension of density functional theory. The site reactivity of the molecules involved in reactions of radical attack to olefins and isocyanide addition to dipolarophiles is rationalized in terms of the orbital and atomic Fukui indices. In such an approach! Toward computation of the chemical descriptors one can indicate the orbital(s) as well as the atom(s) as active centres in the reactions studied. The reactivity descriptors of tiophene, furane and pyrrole are also reported and discussed.

Nelaine Mora-Diez

A Quantum Chemical and CTST Study of the Hydrogen-Abstraction Reaction from Substituted Aldehydes (XCHO: X= F, Cl, H, CH3) by OH radicals: An Explanation for Negative Activation Energies

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The reaction between OH radicals and aldehydes (RCHO) is of interest in atmospheric chemistry. It produces H2O and the RCO radical as the only products, so it can be assumed that the only reaction taking place is the hydrogen abstraction. For acetaldehyde negative activation energy has been measured and there is no unique explanation to this phenomenon.

High level ab initio calculations have been performed to obtain the energy profiles of these abstraction reactions. Geometries and frequencies of all the species involved were calculated at the MP2(FC)/6-311++G(d,p) level and energies were obtained at the CCSD(T)/6-311++G(d,p) level using the previous geometries.

Classical transition state theory (CTST) has been applied for the calculation of the rate constants. Tunneling corrections were calculated after approximating the barriers by an unsymmetrical Eckart function. Some of the calculated low frequencies of the transition structures were treated as free internal rotations with successful results. Theoretical calculations are compared to experiment and a new (complex) mechanism is proposed in which a reversible step is followed by the irreversible hydrogen abstraction from a pre-reactive complex.

Heidi M. Muchall

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Unusual Weak Bonding Interactions in Sulfinyl Amines. N-sulfinyl amines, R-NSO, have the potential to come in two basic geometries, syn and anti. In an “atoms in molecules” study and starting from R=pyrimidinyl, in which both syn and anti are twisted out of the aromatic plane, we have asked if and how to get planar syn and anti geometries in similar compounds. A planar syn is found wherever an in plane O-H interaction is possible, as in R=phenyl. A planar anti can be reached by introducing an in plane S-halogen interaction, as found with R=2,6-dihalo phenyl. The weak bonding interactions will be discussed as well as differences in reactions of syn and anti configurations.

Steven Ole Nielsen

Mixed quantum-classical dynamics (Steve Nielsen & Raymond Kapral)

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For a quantum sub-system coupled to a classical bath we have formulated the governing expressions for dynamical evolution, equilibrium averages and correlation functions as a limiting case of treating both the sub-system and bath in a fully quantum mechanical manner. Numerical evaluation of the resulting expressions requires that we reformulate the basic expressions to be amenable to molecular dynamics and Monte Carlo techniques. Typically we choose to use the adiabatic basis and hence to implement a type of surface hopping treatment. Interesting conceptual problems arise when the bath is complicated or even classically chaotic, and this is the focus of the present study.

Jeff Paci

The Kinetic Energy Distribution of Dissociating Diatomic Molecules.

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We have developed software that enables us to calculate, among other things, the quantum kinetic energy distributions of diatomic molecules as they dissociate in long laser pulses. Heteronuclear and homonuclear diatomics behave very differently. Asymptotically large permanent and transition dipole moments play an important role. Simple models have been developed that allow for a clear physical description of the dynamics that produce the spectra. They also help in explaining the differences observed in heteronuclear versus homonuclear molecules. Classical and semi-classical trajectory calculations have been used to further elucidate the details of the dynamics.

Giuseppe C. Pappalardo

Structural Features and Molecular Assembly of Amorphous Phosphazenic Materials by Combined Theoretical (Molecular Dynamics, MD) and Experimental (Large Angle X-Ray Scattering, EDXD) Techniques: Tris-(2,2´-dioxy-1,1´ binaphthyl)cyclotriphosphazene in the Bulk

Maria E. Amato,a, Ruggero Caminiti,b,Gabino Carriedo, c, Giuseppe M. Lombardo,a, and Giuseppe C. Pappalardo*,a

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NOTES

S. Patchkovskii

Chemical supercomputing on the cheap: 94G Flops computer system at $3680 (cdn) /gigaflop

S. Patchkovskii, R. Schmid, and T. Ziegler, University of Calgary, Calgary, Canada

We report on the construction of one of the largest dedicated computational chemistry resources to date: the COBALT cluster. COBALT (Computers On Benches All Linked Together) consists of 94 Compaq Alpha Personal Workstations 500au connected by a dedicated Fast Ethernet switch. All nodes, which together contain more than 21 gigabytes of memory and 300 gigabytes of scratch disk space are controlled by distributed queuing system (DQS) and can be used as a single computational chemistry resource with PVM and MPI parallel programming libraries. With the peak floating point performance on each node of 1 gigaflops per second, the total construction cost (including all hardware and software) is just cdn$3680 (US$2460 at the February 10, 1999 exchange rate) per gigaflop. Two quantum chemistry applications most heavily used in this laboratory were configured to run in parallel on COBALT. ADF (Amsterdam Density Functional) program is parallelized with PVM message passing library and places only a light load on the communications hardware. It achieves better than 90% parallel efficiency on ten nodes for molecules with 30-40 atoms, and should be able to scale to up to a hundred nodes efficiently for larger systems. PAW (Projector-Augmented plane Waves) ab initio molecular dynamics code is parallelized with the MPI message-passing library. PAW is dominated by fast Fourier transforms and is heavily dependent on efficient inter-node communications. On COBALT, parallel PAW calculations scale efficiently up to four nodes for medium-sized systems (10-20 atoms in ca. 16Å unit cell). Larger number of nodes may be utilized for bigger systems. Overall, COBALT cluster provides a uniquely powerful and inexpensive quantum chemistry resource.

S. Patchkovskii

Extracting quantitative structural information from EPR g-tensors with density functional theory: applications to nitrosoiron(II) porphyrins.

S. Patchkovskii and T. Ziegler, Department of Chemistry, University of Calgary, 2500 University Dr. N.W., Calgary, Alberta.

The recent development of DFT approaches to calculation of electron paramagnetic resonance (EPR) **g**-tensors, it became possible to provide a useful quantitative prediction for the **g**-tensor of a given chemical structure. Combined with theoretical potential energy surfaces, calculated **g**-tensors permit extraction of additional structural and dynamic information from experimental EPR spectra. In the first application of the technique, we examine five- and six- coordinated nitrosoiron(II) porphyrins. In either case, NO ligand is preferably coordinated end-on, with Fe-N-O bond angle of approximately 140^o. In the five-coordinated complex, NO undergoes free rotation around the Fe-N bond. Coordination with the second axial ligand (imidazole) increases barrier for NO rotation to about 1 kcal/mol. Potential energy surface for the dissociation of the weakly-coordinated imidazole ligand is exceptionally flat, with variation of the Fe-N(Im) bond length between 2.0 and 2.5Å changing energy by less than 1 kcal/mol (BP86). Experimental orientations of both axial ligands, as well as Fe-N(Im) bond length, are likely to be determined by intermolecular interactions. In contrast to the total energy, calculated EPR g-tensors are strongly sensitive to the orientation of the NO ligand and the Fe-N(Im) bond length. From comparison of experimental and calculated g-tensors for a range of structures, rhombic EPR signal can be assigned to a static structure with NO oriented towards the meso-C atom of the porphyrin ring, and $R_{Fe-N(Im)}$(2.1Å. Quasi-axial EPR signal is assigned to a partially dissociated structure ($R_{Fe-N(Im)}$(2.5Å), with a freely rotating NO ligand.

S. Patchkovskii

Structural origin of two paramagnetic species in six-coordinated nitrosoion(II) porphyrins revealed by density functional theory analysis of the g-tensors.

S. Patchkovskii and T. Ziegler, Department of Chemistry, University of Calgary, 2500 University Dr. N.W., Calgary, Alberta.

An extensive study of the potential energy surface of model five- and six-coordinated nitrosoiron(II) porphyrins was undertaken. In both cases, NO ligand is preferably coordinated end-on, with Fe-N-O bond angle of approximately 140^{o}. In the five-coordinated complex, NO undergoes free rotation around the Fe-N bond. This motion is strongly coupled to the D_{2d} distortion of the porphyrin ligand. Coordination with the second axial ligand (imidazole) increases barrier for NO rotation to about 1 kcal/mol. Potential energy surface for the dissociation of the weakly-coordinated imidazole ligand is exceptionally flat, with variation of the Fe-N(Im) bond length between 2.0 and 2.5Å changing energy by less than 1kcal/mol (BP86). Experimental orientations of both axial ligands, as well as Fe-N(Im) bond length, are likely to be determined by intermolecular interactions. In contrast to the total energy, calculated electron paramagnetic resonance (EPR) **g**-tensors are strongly sensitive to the orientation of the NO ligand and the Fe-N(Im) bond length. From comparison of the calculated and experimental g-tensor principal components for a range of structures, rhombic EPR signal was assigned to a static structure with NO oriented towards the meso-C atom of the porphyrin ring, and $R_{Fe-N(Im)}$≈2.1Å (Calcd: $\mathbf{g}_{min}$=1.95, $\mathbf{g}_{free}$=2.00, $\mathbf{g}_{max}$=2.04; Expt: $\mathbf{g}_{min}$=1.96-1.98, $\mathbf{g}_{free}$=2.00, $\mathbf{g}_{max}$=2.06-2.08). Quasi-axial EPR signal was assigned to a partially dissociated structure ($R_{Fe-N(Im)}$(2.5Å), with freely rotating NO ligand (Calcd: $\mathbf{g}_{||}$=2.00, $\mathbf{g}_{\perp}$=2.03; Expt: $\mathbf{g}_{||}$=1.99-2.00, $\mathbf{g}_{\perp}$ =2.02-2.03).

Marios Philippopoulos

Molecular Dynamics Study Of A Thermodynamically-unstable Protein.

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The N-terminal drk SH3 domain is a 59-residue protein module that exists in a 1:1 ratio between folded and unfolded states in physiological conditions. The equilibrium between these two states and the dynamic properties of the protein have been extensively characterized experimentally. We have performed nanosecond molecular dynamics simulations of the drk SH3 domain, successively at room temperature and at 348 K, in order to provide further insights into the conformational flexibility of the protein. Dynamical observables calculated from the trajectories are compared with analogous data from NMR spectroscopy.

NOTES

Fabio Pichierri

Pressure-induced Structural Changes In Molecular Crystals From First-Principles Calculations

Fabio Pichierri and Toshikazu Ebisuzaki, Computational Science Division, RIKEN, (The Institute of Physical and Chemical Research), 2-1 Hirosawa, Wako-shi 351-0198, Japan

A variety of novel pressure-induced physico-chemical phenomena have been observed in molecular solids under the effect of compression. Some relevant examples are the pressure-induced polymerization, metallization, and amorphization of molecular crystals. In order to investigate such phenomena, it is necessary to analyze the structural changes that occur inside the compressed crystal lattice. This can be done experimentally by subjecting the crystal to x-ray diffraction analysis while it is being compressed inside a diamond anvil cell (DAC). However, owing to the complexity of the DAC-diffractometer combination, the accuracy of the whole structure determination process decreases as the applied pressure increases. On the other hand, Raman scattering has been very useful in the detection of pressure-induced phase transitions in molecular crystals, by measuring the lattice phonon frequencies, but less in providing informations about the structural changes that occur under compression. An alternative possibility to study the pressure-induced structural changes in molecular crystals is by means of first-principles calculations. This technique, which has been pioneered by Car and Parrinello [1], combines density functional theory (DFT) with molecular dynamics (MD) simulation. In the present poster we will show how first-principles DFT calculations with a plane-wave basis set [2] have been successfully employed to study the structural response of the tetrafluoro-p-benzoquinone (p-fluoranil) crystal up to a pressure of 4 GPa.

References
[1] R. Car and M. Parrinello, Phys. Rev. Lett. 55 (1985) 2471.
[2] M.C. Payne et al., Rev. Mod. Phys. 64 (1992) 1045.

Patrick Pinel

Description of Cyclobutanone on a Mo2C surface: Quantum chemical simulations

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Quantum chemical calculations were made of the electronic structure and vibrational spectra of cyclobutanone-Mo and cyclobutilidiene-Mo model compounds. Those are tought to represent the initial and final states in the interaction of cyclobutanone with a Mo2C surface to form a surface carbene. The calculated vibrational spectra are compared with the experimental ones obtained by reflectance infrared spectroscopy in order to unravel the basic mechanism underlying the dissociative chemisorption process.

Régis Pomès

Molecular Mechanism Of Proton Translocation In Membrane Proteins

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The translocation of protons across biological membranes is fundamental to life. This process is thought to be mediated by a hop-and-turn or “Grotthuss mechanism” involving the chemical exchange of H nuclei in hydrogen-bonded networks or “proton wires”. In membrane proteins, such networks are formed by titratable amino acid groups as well as internal water molecules. We use molecular dynamics simulations to characterise the hop-and-turn mechanism in proton wires comprising single-file chains of water molecules. Gramicidin, a well-characterised cation channel, is a tractable model for more complex biological proton wires. The structural fluctuations governing rapid proton translocation in native gramicidin, in dioxolane-linked channels, and in the presence of methanol are analysed in an attempt to elucidate the molecular basis for the modulation of proton currents in these systems.

Felaniaina Rakotondradany

Hydrogen-bonded azobenzene-based tapes and rosettes: theoretical and experimental studies.

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The design and understanding self-assembled supramolecules is a burgeoning area of research. Hydrogen bonds have been used extensively to build molecular tapes and hexameric rosettes. Azobenzenes undergo a trans-cis isomerization at 310 nm and revert to the trans conformer upon heating or irradiation at 440 nm. The most stable (trans) azodibenzoic acid should form linear tapes. The cis photoisomer can yield all-cis tapes but also novel hexameric rosettes thus amplifying the effect of light.

PM3 semi-empirical calculations from monomers to hexamers suggest that trans isomers form tapes and cis isomers rosettes. Azodibenzoic acid is obtained by reducing p-nitrobenzoic acid. Preliminary NMR studies indicate a poor photoisomerization yield in DMSO-d6 at room temperature. UV irradiation at lower temperatures is envisaged to optimise the photoisomerization yield. The poorly soluble dicarboxylic acid is also synthetically modified using long alkoxy chains.

Kathryn Rankin

Catalysis Mediated by Hydrogen Bonding

Kathryn N. Rankin, James W. Gauld and Russell J. Boyd, Department of Chemistry, Dalhousie University, Halifax, N.S., B3H 4J3

The use of hydrogen bonding, an essential component of the structure and function of biological molecules, in the stabilization of reaction intermediates and transition structures is well established. Recently, Tominaga, Konishi and Aida1 reported the catalysis of aminolysis of 6-chloropurine and related species by derivatives of the nucleobase uracil. Since this catalytic behavior was proposed to occur as a result of multiple hydrogen bonding interactions, the model reaction of aminolysis of 6-chloropyrimidine was examined to provide a rationalization for the role of hydrogen bonding interactions.

The isolated barrier to aminolysis is found to require 138.1 kJ mol-1. However, upon addition of H2CO, an electron-donating group which interacts with NH3, this barrier is reduced to 112.2 kJ mol-1. Utilizing HCO-NH2, which contains electron-donating and electron-withdrawing groups, as the base reduces the barrier by an additional 17 kJ mol-1. Thus, the aminolysis of 6-chloropyrimidine, as mediated by hydrogen bonding, provides a clear example of the catalytic possibilities associated with hydrogen bonding.

1 Tominaga, M.; Konishi, K.; Aida, T. J. Am. Chem. Soc. 1999, 121, 7704.

Mathieu Roberge

Molecular Modelling of Axially Drawn Amorphous Polyethylene Terephthalate by Parrinello-Rahman Molecular Dynamics.

Mathieu Roberge and Josée Brisson, CERSIM (Centre de recherche en sciences et ingénierie des macromolécules) and Département de chimie, Faculté des sciences et de génie, Université Laval, Québec, Québec Canada G1K 7P4

Although numerous experimental studies have dealt with PET drawing in the past decade, the molecular mechanisms involved are still unclear. Molecular Dynamics (MD), particularly the approach developed by Parrinello and Rahman for crystals, is a invaluable tool to achieve simulation of the deformation process. Due to the exponential growth in computer speed, it is now possible to use this method for very large systems such as amorphous phases. An amorphous model of the polyethylene terephthalate (PET) has been created with the chain propagation method. The Parrinello-Rahman technique was then employed to study its constant load deformation and the initial relaxation process associated with the withdrawal of the stress. Simulation of drawing up to 400% were performed for various combinations of pressure, temperature, cell mass and density. Subsequent relaxation was showed to be many order of magnitude faster than the first experimentally observable relaxation process, which is in agreement with the hypothesis of a mixed deformation-relaxation process during experimental stretching measurements. A review of the model creation and deformation will be given, along with some results from the relaxation process.

Alain Rochefort

Electrical Resistance of Molecular Wire: Supermolecule or 1-D System ?

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The future of integrated circuits is irremediably directs towards the production of nanoelectronic or moletronic components in order to across the technological limit of materials. This will make it possible to increase the number of transistors per unit of area and thus to increase the power of the current chips. In this regards, carbon nanotubes appear an interesting alternative because of their variables electrical properties. In this poster, I will give an overview of the computational methodology used to evaluate the electrical transport properties in molecular species, especially in metallic carbon nanotubes. Although the latter is considered to be a perfect conductor which are similar to 1-D systems (like wire), I will show exemples (size, deformation, doping) where the material shows a transition from 1-D to 0-D, i.e. showing typical molecular caracteristics.

Christopher F. Rodriquez

Proton Migration and Tautomerism in Protonated Peptides.

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Proton migration in protonated glycylglycylglycine (GGG) has been investigated at B3LYP/6-31++G(d,p). On the protonated GGG free energy hypersurface seventeen critical points have been characterized, ten as minima and seven as first-order saddle points. Transition-state structures for the interconversion between eight of these minima are reported starting from a structure in which there is protonation at the amino nitrogen of the N-terminus to the formation of protonated 5-oxazolone (the b2 ion) and glycine. Individual free energy barriers are small, ranging from 4.3 to 18.1 kcal mol-1. The most favourable site of protonation on GGG is the carbonyl oxygen of the N-terminal residue. This isomer is stabilized by a hydrogen bond of the type O-H•••N, resulting in a compact five membered ring. Another oxygen-protonated isomer with hydrogen bonding of the type O-H...O, resulting in a seven membered ring, is only 0.1 kcal mol-1 higher in free energy. Protonation on the N-terminal nitrogen produces an isomer that is about 1 kcal mol-1 higher in free energy than isomers resulting from protonation on the carbonyl oxygen of the N-terminal residue. The calculated free energy barrier to generate the b2 ion from protonated GGG is 32.5 kcal mol-1. The calculated basicity and proton affinity of GGG from our results is 216.3 and 223.8 kcal mol-1. This is 3 -4 kcal mol-1 lower than those from previous calculations and is in excellent agreement with recently revised experimental values.

Nino Russo

Interaction of Mo and Mo2 with NH3,C2H4 and C3H6

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Density functional computations were performed on Mon-X (n=1,2;X=NH3, C2H4,C3H6)systems in order to obtain information on molecular geometry, coordination modes, binding energies and vibrational frequencies for these complexes. The exchange-correlation functionals used were PP, BP, B3LYP and B3PW91 coupled with TZVP and LANL2DZ basis sets. Results show that NH3 is bonded only with Mo2, while C2H4 and C3H6 with Mo. The computed binding energies are in agreement with the available experimental data. The nature of metal-ligand bond was elucidated using different theoretical tools.

Abdulwahab Sallabi

Structures and Stabilty Of Carbon Monoxide Physisorbed On MgO: Descending The Devil's Staircase

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Metropolis Monte Carlo simulations are performed to study the structures and stability of CO molecules physisorbed on the MgO(001) surface. In agreement with experiments, MC simulations confirm that below 41 K the CO molecules form a c(4x2) structure. The unit cell contains three CO molecules; two bridging molecules tilted in opposite directions by the same polar angle of 31° with respect to the surface normal and a third molecule perpendicular to the surface. Both sites are localized near Mg2+ ions. At 41 K and conditions of low pressure, the c(4x2) phase undergoes a transition to a less dense disordered phase via the expulsion of molecules. A further transformation to a p(3x2) phase is possible by converting tilted to perpendicular molecules. A model to test the relative stability of the c(4x2) and p(3x2) phases shows that at sufficiently high pressures and temperatures the p(3x2) phase is more stable than the c(4x2) phase as found experimentally. We propose that a sequence of transitions through a set of (nx2)-type structures with ever decreasing density is possible under suitable conditions of temperature and pressure. This sequence of transitions is an example of devil's staircase phenomenon as has been suggested by LEED experiments.

Mihai Scarlete

Phase Transfer of Chemical Oscillations via Fluid Dynamics. MapleV-Assisted Simulation of Polymer-Assisted Vapor Deposition under Cylindrical Symmetry.

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Polymer-Assisted Vapor Deposition method (PA-VD) was developed in our group for the synthesis of thin ceramic and semiconductors layers on large surfaces, in conditions rendering Chemical Vapor Deposition inapplicable. For example, a specific characteristic of the procedure is the fast deposition rate of silicon carbide on large, irregular or dielectric substrates. The method uses the gaseous species generated via fragmentation of various organo-silicon polymers exposed to specific thermal and chemical conditions. A recent development is the induction of space-oscillations in the thickness, conductivity or chemical composition of thin films of Nitrogen-doped silicon carbide deposited on electronic grade alumina and silicon single crystal wafers from poly(dimetyl)silane. The procedure involves the control of the gas flow pattern at a certain partial pressure of ammonia. This way, a 2D-array of precisely positioned areas of SiC-films with different characteristics may be created on a substrate. The substrate becomes eventually a "library-substrate" that could be used in the experimental design and optimization of semiconductor SiC devices. The paper presents the computational results obtained in the modeling process of the flow dynamics under appropriate conditions for maximization of the oscillatory process under simultaneous influence of the gradient-controlled flow regime and chemically controlled diffusion in cylindrical furnaces.

Hartmut Schmider

Monitoring Reactions by various Density-Based Surfaces

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Density-based surfaces of the Electron Localization Function (ELF), Localized Orbital Locator (LOL), Shannon Entropy Densities, Parity Function, and Laplacian of the charge density, in position and momentum space, are monitored following the Intrinsic Reaction Paths (IRC's) of various reactions. Classical chemical concepts of bond breaking and formation may in some case be illustrated by means of such surfaces, furthermore, stages of the reaction may be established and classified more easily then by solely analyzing the energy profile and geometrical parameters.

Jiushu Shao

Semicalssical forward-backward formalism of Heisenberg operators

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Initial-value phase-space integral representations for the Heisenberg operator are obtained by employing the forward-backward evolution methodology. Within the stationary phase approximation, the Wigner representation of all the semiclassical Heisenberg operators are reduced to the classical Wigner formula.

Tamer Shoeib

Solvent-Assisted Rearrangements between Tautomers of Protonated Peptides.

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The presence of an interacting water or methanol has been shown to catalyze the 1,3-proton shift in a peptide linkage between the tautomers of protonated formamide and glycylglycylglycine. Density functional theory calculations at the B3LYP/6-31++G(d,p) level of theory show that for glycylglycylglycine the forward barrier of this shift decreases from a free energy at 298 K of 39.6 kcal/mol in the absence of solvent, to 26.7 kcal/mol in the presence of water, and to 22.0 kcal/mol in the presence of methanol. Protonation at the amide nitrogen of the second residue results in a large increase in the C-N bond distance from 1.336 to 1.519 Å, whereas protonation at the carbonyl oxygen leads to a decrease in the C-N bond distance from 1.336 to 1.321 Å. Solvent-catalyzed tautomerism may play an important role in the fragmentation of electrosprayed, protonated peptides in the gas-phase.

Tamer Shoeib

Proton Migration and Tautomerism in Protonated Peptides

Proton migration in protonated glycylglycylglycine (GGG) has been investigated at B3LYP/6-31++G(d,p). On the protonated GGG free energy hypersurface seventeen critical points have been characterized, ten as minima and seven as first-order saddle points. Transition-state structures for the interconversion between eight of these minima are reported starting from a structure in which there is protonation at the amino nitrogen of the N-terminus to the formation of protonated 5-oxazolone (the b2 ion) and glycine. Individual free energy barriers are small, ranging from 4.3 to 18.1 kcal mol-1. The most favourable site of protonation on GGG is the carbonyl oxygen of the N-terminal residue. This isomer is stabilized by a hydrogen bond of the type O-H...N, resulting in a compact five membered ring. Another oxygen-protonated isomer with hydrogen bonding of the type O-H•••O, resulting in a seven membered ring, is only 0.1 kcal mol-1 higher in free energy. Protonation on the N-terminal nitrogen produces an isomer that is about 1 kcal mol-1 higher in free energy than isomers resulting from protonation on the carbonyl oxygen of the N-terminal residue. The calculated free energy barrier to generate the b2 ion from protonated GGG is 32.5 kcal mol-1. The calculated basicity and proton affinity of GGG from our results is 216.3 and 223.8 kcal mol-1. This is 3 - 4 kcal mol-1 lower than those from previous calculations and is in excellent agreement with recently revised experimental values.

Alexandre A. Shvartsburg

New Hybrid Method To Calculate Ionic Mobilities Involving The Scattering On Atoms And On Electron Density Surfaces

Alexandre A. Shvartsburg, Bei Liu, K.W. Michael Siu, and Kai-Ming Ho, (Department of Chemistry, York University, Toronto, Ontario and USDoE Ames Laboratory, Ames, Iowa, USA)

A recently developed method to evaluate gas-phase ionic mobilities by scat-tering on electron density isosurfaces (SEDI) has been tested for carbon cluster ions. The investigation has covered species belonging to all major structural families revealed in the drift tube studies (chains, rings, graphite sheets, and fullerenes). Relative cross sections of C_n cations and anions predicted by SEDI are in excellent agreement with the measure-ments, but the absolute values could not be fit for either charge state. This happens because SEDI ignores the long-range ion-buffer gas interaction critical for many systems including carbon clusters. To overcome this, we propose a new technique to evaluate mobilities by coupling SEDI with trajectory calculations. This approach allows one to introduce the repulsive interaction accurately and still account for the attractive part of the potential. This hybrid SEDI-TC treat-ment is demonstrated to substantially outperform all models previously described in reproducing both absolute and relative mobilities of C_n anions and cations.

Ming-Der Su

Theoretical Study of Oxidative Addition and Reductive Elimination of 16-Electron d4 [n]-Metallocenophane Complex.

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We have chosen eight [n]-metallocenophane complexes, including a systematic variation in the geometrical structures and metals, to investigate oxidative additions as well as the reductive eliminations by using the B3LYP/LANL2DZ level of theory.

Considering the geometrical effect and the nature of the metal center, the following conclusions therefore emerge: for 16-electron [n]-metallocenophane complex, a larger bending angle (Cp-M-Cp) as well as a heavier transition metal center (such as W) should be a potential model for the oxidative addition of saturated C-H bonds. Conversely, a parallel ring structure and a lighter transition metal center (such as Mo) would be a good candidate for reductive coupling of C-H bonds. Our model calculations suggest that a methane s-complex intermediate should be formed between [n]-metallocenophane and methane, which should play a major role in either oxidative additions or reductive eliminations. Moreover, we show that both electronic and steric effects play a significant role in the preference for sCH2 approach, from which one may predict the formation and stabilities of the regio- and stereoselective insertion products.

Masanori Tachikawa

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The Positron Molecular Compounds by the Fully Variational Molecular Orbital Method.Recently the atomic or molecular systems containing the antiparticle such as a positron or an antiproton are attracting the interest of many researchers in both experimental and theoretical fields. In this paper I present the results of

calculation for the positron - molecule compound, by ab initio fully variational molecular orbital (FVMO) method with consideration of correlation effect [1][2].In this FVMO calculation, all variational parameters such as exponents and centers of Gaussian-type function (GTF) for electronic and positron basis sets are optimized as well as linear combination of GTF (LCGTF) and configuration interaction (CI) coefficients. We found that the FVMO method is the powerful technique, since the basis sets of other quantum light particles, such as positron, muon, or proton, which basis functions are not proposed variationally yet, can be determined simultaneously, as well as the electronic basis functions.

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[2] M.Tachikawa, K.Mori, K.Suzuki, and K.Iguchi, Int.J.Quant.Chem. 70, 491 (1998).

Seiichiro Ten-no

I Developments in the integral equation theory for molecular liquids II. A method for a feasible treatment of electron correlation cusps.

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I. We develop an integral equation theory based on the partial wave expansion of the molecular Ornstein-Zernike equation. The theory provides a rigorous and transparent framework for multiple site treatments of molecular fluids. We examine free energy functional and closure expressions with pilot calculations.
II. A method is developed for accelerating the convergence of reproducing the dynamic correlation effects. Employing a frozen Gaussian geminal (FROGG), we parameterized an effective Hamiltonian such that the Coulomb interaction is compensated at short inter-electronic distances. The extra part of the effective Hamiltonian is short-ranged, spin-free, size-consistent, and universal to states of interest. Thus the method is suitable for calculating large molecular systems accurately.

Wei Quan Tian

Tests of Density Functional Theory: Theoretical Investigations of the Reaction of Oxygen (3P) with Benzene and Isomerization of Benzene Oxide

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We have studied the addition of an oxygen atom O(3P) to benzene in order to analyze the bonding in transition states and products by density functional theory and by conventional ab initio methods. Possible pathways for the reaction of an oxygen atom with benzene and for the isomerization of the benzene oxide products have been discussed in detail. Available experiment data are rationalized. The performance of various exchange-correlation functionals in density functional theory (BHandHLYP, B1LYP, B3LYP, BLYP and MPW1PW91) was analyzed for molecular properties and compared with results from MP2 theory. The role of exact-exchange in accurate predictions of the structure and energetics of these molecular systems has been considered in detail.

Hiroaki Tokiwa

Origin of Reactivity and Selectivity of Hybrid-type Zincates

†Hiroaki Tokiwa, Kei Machida, The Department of Chemistry, Rikkyo University
Masanobu Uchiyama, and Yoshinori Kondo, Contribution from the Graduate School of Pharmaceutical Sciences, Tohoku University

Organozincate complexes have been extensively used in recent organic synthesis. The halogen or hydrogen-zinc exchange reaction (metallation), reduction, and oxidation, not only the alkylation reaction, using various zincates have recently been realized. From the view point that center metal plays an active part in the individual reaction, some metalloenzymes are also microscopically regarded as a kind of ate complex. Namely, we can postulate Zn(II)-ate complexes as the simplest model of zinc enzymes. The transference aptitude of various group on Zn was already experimentally revealed and utilized such aptitude also produced a new catalytic reducing system of carbonyl compounds. The fact that the reaction catalytically proceeds in the zinc enzyme, experiments are at least due in part to the characteristic feature that the magnitude of the transference aptitude remarkably varies groups on Zn. The origin of reactivity and selectivity of hybrid-type-zincates ($R_2Zn(H)^-Metal^+$) has been investigated using *ab initio* and density functional theory (DFT) calculations.

Alejandro Toro-Labbe

Determination of Hydrogen Bond Energies from the Estimate of Global Electronic Properties through the Sanderson's Principle

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We use the Sanderson's geometric mean equalization principle for the electronegativity to derive expressions for molecular hardness and its derivative. Bond energies of fourteen molecules and bimolecular complexes have been rationalized in terms of these electronic properties. It has been found that the conditions of maximum hardness and minimum polarizability complement the minimum energy criterion for stability of molecular aggregates.

Jean-Francois Truchon

Construction of a Force Field Based on DFT Molecular Electrostatic Potential and its Use in QM/MM Methodology

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Improving the electrostatic part of a force field, especially its anisotropic and polarisable components,is very important when one is interested in precision of certain interactions. However, the way of doing this is still not clear. In this work, we use the molecular electronic density obtained with density functional theory (DFT) to describe the molecular electrostatic potential via cumulative atomic multipolar moments (CAMM) and MEP fitting. We go beyond the charges up to the atomic quadrupole moment. Early results are presented and the perspective of using this kind of force field in a DFT based QM/MM methodology is discussed.

Kumar Vanka

A Density Functional Study of the Effect of Counterions and Solvents on the Activation of the Olefin Polymerisation Catalyst $(1,2Me_2Cp)_2ZrMe^+$

Kumar Vanka, Mary Chan,Cory Pye and Tom Ziegler, Department of Chemistry, University of Calgary, Calgary, Alberta Canada T2N 1N4.

Cationic metallocene compounds of the type Cp_2MR^+ ($Cp = C_5H_5$, R= CH_3, C_2H_5 etc.) have been the subject of intense scrutiny over the past few years due to their ability to act as olefin polymerisation catalysts. The role of solvents, activators and counterions in influencing the activities of these metallocene compounds has been extensively investigated in experimental studies but little theoretical work has been done in this area. The present investigation studies the activation of the catalyst precursor $(1,2\text{-}Me_2Cp)_2ZrMe_2$ by a series of borane and aluminum based activators to form the corresponding ion-pairs. The relative ease of dissociation of the ion-pairs thus formed is also analysed. The role of the solvent (toluene) in the activation process is considered by studying the possibility of the formation of solvent separated ion-pair species in solution. The next part of the work consists of a study of the inhibitive processes that are possible at the start of the polymerisation i.e. various side reactions that are possible betweeen the cationic catalyst and other species that exist in solution, leading to dormant products. The competition between the monomer and the solvent for coordination to the cation in the presence of the counterion is also investigated. The calculations were carried out at the NL-P/LDA level. Solvation effects were incorporated using the Conductor Like Screening Model.

Dr. Vladislav Vassiliev

Determination of the Effective Dielectric Constant From the Accurate Solution of the Poisson Equation

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Simulations involving explicit water are very expensive computationally, which makes its applications to practical problems such as drug design very difficult. Driven by these computational exigencies, a number of approximate continuum approaches have been developed but only one of these methods, the Poisson, is based upon rigorous physics. However, obtaining accurate numerical solutions to the Poisson equations for the large systems such as proteins still has a significant computational cost, so efforts have been made to develop inexpensive continuum solvation models to be used for this purpose. Two of them, constant dielectric (CD) function and distance dependent dielectric (DDD) function, are the most popular and widespread in the Molecular Mechanics simulations of the large molecular systems. At the same time few attempts have been done to assess their reliability for large systems. One of the difficulties here is that we can’t compare directly electrostatic energies obtained using CD or DDD functions with the reference solvation free energies, for example, from the Poisson method.Thus, the goal of our study was to find a direct way how to determine an effective dielectric constant in the CD and DDD approaches based of the reference Poisson calculations.

Nick H. Werstiuk

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An ELF (Electron Localization Function) Study of Methyl-Substituted 2-Bicyclohexyl[2.2.1]heptyl Cations. N.H. Werstiuk and S. Noury. Department of Chemistry, McMaster University, Hamilton, Ontario Wave functions obtained at the Becke3LYP, Becke3PW91 and MP2 levels of theory are used in a topological analysis of the Becke-Edgecombe electron localization function (ELF) with the Silvi suite of programs. Partioning of the molecular space of the cations into basins of attractors yields information on the nature of the shared valence basin interactions at the C1-C2-C6 face of these so-called nonclassical cations. We find no evidence for bridging, a finding which is nicely in accord with the results of an AIM (Atoms in Molecules) study on these species.

Stephen K. Wolff

Calculation of the DFT-GIAO NMR Shifts With Inclusion of Relativistic Effects: Pauli and ZORA formalisms.

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A formulation for the calculation of nuclear magnetic resonance (NMR) shielding tensors based on density functional theory (DFT) is presented. Both the relativistic Pauli and relativistic Zero Order Regular Approximation (ZORA) formalisms have been implemented. Gauge-including atomic orbitals (GIAO) and a frozen-core approximation are used. ^{1}H NMR shifts of hydrogen halides, ^{13}C NMR shifts of 5d transition metal carbonyls, and ^{199}Hg shifts of various mercury molecules have been calculated and show good agreement with experiment.

Troy W, Wymore

Computational Studies of Aldehyde Dehydrogenase

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Results from recent molecular dynamics simulations of aldehyde dehydrogenase which involves the enzyme dimer, two NAD cofactors, the benzaldehyde substrate and over 10K water molecules for a total of 56 K atoms will be presented. The analysis focuses on the properties of conserved residues known through extensive sequence analysis of this enzyme family and on the conformation and dynamics of the NAD cofactors. In addition, results from 1) Poisson-Boltzmann calculations to assign the protonation state of key residues near the active site and 2) the homology derived structures of some unknown aldehyde dehydrogenase structures will be presented.

Tomoyuki Yamamoto

First-principles calculations of τ (hcp) and τ (fcc) cobalt at high-pressure

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It is believed that the Earth's core is mainly composed of iron-dominated alloys in which cobalt and/or nickel are possible elements as minor components. Very recently, structural phase transition of cobalt from τ (hcp) to τ (fcc) phases at a pressure between 105 and 150 GPa was found experimentally [1]. Here the first-principles calculations of cobalt with hcp and fcc structures are performed changing these volumes. In these calculations, the Full-potential Linearized Augmented Plane Wave (FLAPW) package [2] is employed within the spin-polarized Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA). Resulting lattice constants for both hcp and fcc structures at ambient conditions agree with the observed ones, and the transition pressure from hcp to fcc phases, estimated by total energies as a functions of volume, falls within an experimental range. The magnetic properties of hcp and fcc cobalt under high-pressure conditions are also discussed.

[1] C.S. Yoo et al., Phys. Rev. Lett. 84 (2000) 4132.
[2] P. Blaha, K. Schwarz, and J. Luitz, WIEN97, A Full Potential Linearized Augmented Plane Wave Package for Calculating Crystal Properties (Karlheinz Schwarz, Techn. Universität Wien, Austria), 1999. ISBN 3-9501031-0-4.

Eva Zurek

Modeling MAO (Methylaluminoxane)

Eva Zurek, Tom Woo and Tom Ziegler, Department of Chemistry University of Calgary, Calgary, Alberta, Canada T2N 1N4

Density Functional Theory (DFT) has been used to calculate the energies of over 30 different methylaluminoxane (MAO) caged structures with the general formula $(MeAlO)_n$, where n ranges from 4 to 16. Via the use of a least-squares fit a formula has been devised which predicts the relative energies of the MAO structures reasonably well. These energies in conjunction with frequency calculations based on molecular mechanics have been used to estimate the enthalpies, free energies and equilibrium constants for the general equilibrium $(MeAlO)_{n1}$+ $(MeAlO)_{n2}$ τ $(MeAlO)_{n1+n2}$ This procedure makes it possible to estimate the relative abundence of $(MeAlO)_n$ as a function of n. Similar procedures have been used to study the equilibrium between $Al_2(CH_3)_6$ and MAO in the equilibrium : $(AlCH_3)_m(MeAlO)_n$ τ: $(AlCH_3)_{m-2x}(MeAlO)_n$ $+xAl_2(CH_3)_6$ and the relative abundence of $(AlCH_3)_m(MeAlO)_n$ for different m. We have further shown from topological arguments that the MAO cage structure contains a limited number of squares compared to hexagons and octagons. It is futher suggested that the limited number of squares with their strained and reactive Al-O bonds can explain the high molar Al:(Catalyst) ratio required for activation. The mode of activation as well as the way in which $AlCH_3$ is coordinated to MAO is also discussed.

NOTES

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4th Canadian Symposium on Computational Chemistry - Programme

	Sun, July 30	**Mon July 31**	**Tues Aug 1**	**Wed Aug 2**	**Thurs Aug 3**
8:20 - 8:30		**Welcome/introduction**			
8:30 - 10:20	***Registration all day***	***Scientific session: Advances in quantum chemistry methodologies***	***Scientific session: Advances in force fields***	***Scientific session: Cheminformatics***	***Scientific session: Materials modeling***
8:30 - 9:00		Bill Goddard, Cal Tech, USA	Peter Kollman, U. of California, SF, USA	Anton Hopfinger, U. of Illinois, USA	John Tse, NRC, Canada
9:00 - 9:30		Axel Becke, Queens U., Canada	Alex MacKerrell, U. of Maryland, USA	Eugene Fluder, Merck & Co., Rahway, NJ, USA	Rajiv Kalia, Louisiana State U., USA
9:30 - 10:00		Rod Bartlett, U. Of Florida, USA	Thomas Halgren Schrodinger Inc, USA	Christopher Williams, Chemical Computing Group Inc., Canada	Otto Sankey, Arizona State, USA
10:10 - 10:20		Hot topic	Hot topic	Hot topic	Hot topic
10:20 - 10:40		coffee	coffee	coffee	coffee
10:40 - 12:30		***Scientific session: Advances in classical and quantum dynamics***	***Scientific session: QM/MM methodologies***	***Scientific session: coring functions***	***Scientific session: New hardware and software paradigms***
10:40 - 11:10		David Clary, U. College, London, UK	Tom Ziegler, U. of Calgary, Canada	Ingo Muegge, Bayer Research Center, USA	Daniel Lidar U. of California, Berkeley, USA
11:10 - 11:40		Raymond Kapral, U. of Toronto, Canada	Alain St-Amant, U. of Ottawa, Canada	David Pearlman, Vertex Pharmaceuticals, USA	Toshikazu Ebisuzaki, RIKEN, Japan
11:40 - 12:10		David Wardlaw, Queens U., Canada	Martin Field, IBS, Grenoble, France	Gennady Verkhivker, Agouron Pharmaceuticals, USA	Dennis Newns, Yorktown Heights, USA
12:10 - 12:30		Hot topic	Hot topic	Hot topic	Conclusion
12:30 - 2:00	***Lunch***	***Lunch***	***Lunch***	***Lunch***	
2:00 - 5:00	***Free time/exhibits***	***Free time/exhibits***	***Free time/exhibits***	***Free time/exhibits***	
5:00 - 6:00		***Poster 1, 2min.***	***Poster 2, 2min.***	***Poster 3, 2min***	
6:00 - 7:30		***Dinner***	***Banquet***	***Dinner***	
7:00	***Welcome cocktail/ reception***				
7:30 - 9:20		***Scientific Session: Electron/proton transfer problems***		***Scientific Session: Free energy of solvation***	
7:30 - 8:00		Nancy Makri, U. of Illinois, USA		Dave Case, Scripps, USA	
8:00 - 8:30		Sharon Hammes-Schiffer, Pennsylvania State U., USA		Anthony Nicholls, Open Eye Software,USA	
8:30 - 9:00		Jeremy Schofield, U. of Toronto, Canada		Enrico Purisima, NRC, Canada	
9:00 - 9:20		Hot topic		Hot topic	
9:20 -		***On-going poster sessions/ exhibits***	***On-going poster sessions/ exhibits***	***On-going poster sessions/ exhibits***	