CSTC 2004

15th CANADIAN SYMPOSIUM ON THEORETICAL CHEMISTRY

Le 15ième symposium canadien de chimie théorique

Hôtel Le Chantecler
Sainte-Adèle, Québec, Canada
July 10-14, 2004

Abstracts and Program

Welcome

We would like to extend to you a warm welcome to CSTC 2004, the 15th Canadian Symposium on Theoretical Chemistry. The CSTC conferences have been bringing together theoretical chemists from Canada and around the world for almost forty years. Previous meetings have been held in Edmonton (1965), Montréal (1967), Toronto (1969), Vancouver (1971), Ottawa (1974), Fredericton (1977), Banff (1980), Halifax (1983), Toronto (1986), Banff (1989), Montréal (1992), Fredericton (1995), Vancouver (1998), Ottawa (2001), and now in Sainte-Adèle, Quebec.

Ste-Adèle is the first of the Laurentian resort towns as one travels north of Montréal. The Laurentian district is a vast playground of forests, rolling hills and mountains, rivers and lakes, and resort hotels such as Hôtel Le Chantecler, site of CSTC 2004. In winter this area is famous for skiing. In summer, hiking, swimming, boating, cycling, golf, wilderness camping and many other activities are enjoyed here. Spectacular fall colours, as depicted on the cover photo, are the highlight of the fall season.

From July 10 to 14, 2004, we hope you'll savour the atmosphere of this Laurentian resort hotel, as well as the science of the 15th CSTC. The program of invited lectures focuses on recent developments in quantum chemistry and dynamics. The contributed poster presentations cover a broad range of theoretical and computational chemistry. We hope you'll enjoy your stay, and that you'll be inspired by the scientific discourse as well.

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Invited Speakers

Abstracts in presentation order

Beyond the Quantum Instanton Model: Computing Thermal Reaction Rates from Higher Derivatives of the Zero Time Flux Correlation Function

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The recent 'quantum instanton' model that has proved quite useful for computing thermal rate constants of chemical reactions is generalized by employing higher order derivatives of the flux-flux autocorrelation function at t = 0. [These are computed using recent developments by Doll and Predescu in Monte Carlo path integration for the Boltzmann operator.] Rate constants are obtained to better than 10% accuracy over a wide range of temperature.

Ab initio molecular dynamics study of the mechanism of 1,3-butadiene attachment to the Si(100)2×1 surface

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A basic understanding how organic molecules attach to semiconductor surfaces could open up new potential applications in the areas of nanoscale devices, in which organic layers of controllable thickness contain molecules that serve as passive or active components. In this talk, we report on our recent *ab initio* molecular dynamics investigations of the mechanism of 1,3-butadiene attachment to the Si(100)2×1 surface. These calculations employ gradient-corrected Kohn-Sham density functional theory in conjunction with a plane-wave basis expansion of the orbitals, novel new techniques developed by us for properly treating surface boundary conditions within this framework [1], and a field-theoretic approach to the generation of maximally localized Wannier functions as the dynamics proceeds [2]. In agreement with recent experiments [3], we find several additional products, including a Diels-Alder [4+2] addition, in which a surface dimer acts as a dienophile, and two other products, in which the butadiene either bridges two dimers within the same row or two dimers in different rows. A detailed analysis of the electronic structure strongly suggests that the mechanism of the Diels-Alder reaction occurs in an asymmetric manner via the formation of an intermediate carbocationic state. A similar mechanism is found to govern the formation of the other two addition products as well.

[1] P. Minary, M. E. Tuckerman, K. Pihakari and G. J. Martyna, *J. Chem. Phys.* **116**, 5351 (2002).
[2] J. W. Thomas, R. Iftimie and M. E. Tuckerman, *Phys. Rev. B* **69**, 125105 (2004); R. Iftimie, J. W. Thomas and M. E. Tuckerman, *J. Chem. Phys.* **120**, 2169 (2004).
[3] L. C. Teague and J. J. Boland, *J. Phys. Chem. B* **107**, 3820 (2003).

A Nonempirical Density Functional Straddling the Paradigm Densities of Quantum Chemistry and Condensed Matter Physics

John P. Perdew

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On the Jacob's Ladder of density functional approximations for the exchange-correlation energy, each higher rung adds another local ingredient which can be used to satisfy further exact constraints. The first rung is the local spin density approximation, which uses the local spin densities, and the second is the generalized gradient approximation (GGA), which adds the gradients of the spin densities. The nonempirical functionals on the first two rungs are controlled extrapolations from the limit of slowly-varying density, a paradigm of condensed matter physics. The third rung or meta-GGA further adds the Kohn-Sham local kinetic energy density. Its nonempirical realization is the TPSS meta-GGA [1], a controlled interpolation between the slowly-varying density and the one- or two-electron density, a paradigm of quantum chemistry. I will review the construction [1] of this functional and its mostly-successful numerical tests for atoms [2], molecules [3-5], and solids [6].

[1] J. Tao, J.P. Perdew, V.N. Staroverov, and G.E. Scuseria, *Phys. Rev. Lett.* **91**, 146401 (2003); J.P. Perdew, J. Tao, V.N. Staroverov, and G.E. Scuseria, *J. Chem. Phys.* **120**, 6898 (2004).

[2] V.N. Staroverov, G.E. Scuseria, J.P. Perdew, J. Tao, and E.R. Davidson, submitted to *Phys. Rev. A.*

[3] G.I. Csonka, A. Ruzsinszky, J. Tao, and J.P. Perdew, *Int. J. Quantum Chem.*, to appear.

[4] V.N. Staroverov, G.E. Scuseria, J. Tao, and J.P. Perdew, *J. Chem. Phys.* **119**,12129 (2003).

[5] F. Furche and J.P. Perdew, in preparation.

[6] V.N. Staroverov, G.E. Scuseria, J. Tao, and J.P. Perdew, *Phys. Rev. B* **69**, 075102 (2004).

What is μ?

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The "exchange-correlation derivative discontinuity" has drawn quite considerable attention recently and many research groups have been designing new exchange-correlation density functionals and potentials based on such theoretical results. The backbone of the "exchange-correlation derivative discontinuity" arguments heavily relies on a particular value of the chemical potential, $\mu = -(I+A)/2$, which is the negative of Mulliken's electronegativity. Here, I and A are the first ionization potential and the first electron affinity of a bounded quantum system under investigation, respectively. Unfortunately, there are already at least six different values of the chemical potential within the present DFT framework. Naturally, one would like to ask the following questions: Which one is the exact value of the chemical potential? Does the exact value of the chemical potential differ from the one commonly employed in the theory of the "exchange-correlation derivative discontinuity"? What are the consequences if they are indeed distinct? To gain an understanding of these issues, we will go through a theoretical journey in search of the correct definition of the functional derivative of the universal density functional in Fock space, which yields the correct definition of the chemical potential at an integer number of electrons. As a consequence, we provide a mathematically rigorous confirmation for the "derivative discontinuity" initially discovered by Perdew *et al.* [Phys. Rev. Lett. **49**, 1691 (1982)]. However, the functional derivative of the exchange-correlation functional is continuous with respect to the number of electrons in Fock space, *i.e.* there is no "derivative discontinuity" of the exchange-correlation functional at an integer number of electrons. For any external potential converging to the same constant at infinity in all directions, we find that the exact value of the chemical potential at an integer number of electrons is the negative of the first ionization potential, $\mu = -I$, not the popular preference of the negative of Mulliken's electronegativity.

Localized orbitals and electron correlation

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Some of the issues associated with developing fast methods for the wavefunction-based description of electron correlation will be re-examined in this talk.

The first issue is the determination of localized molecular orbitals. In systems with a gap, it is well known that the occupied molecular orbitals can be localized. One natural definition of localized orbitals are those that maximize self-interaction, as first advocated by Ruedenberg. We shall describe a new approach to finding localized orbitals, which is well-suited to the treatment of very large molecules, based upon a surrogate function which can be globally maximized.

The second issue we shall examine is a fast and simple form for the electron correlation energy. A modified form of second order Moller-Plesset theory (MP2) is explored, which is based on scaling only the opposite spin correlation energy. Remarkably, relative energies calculated with this modified MP2 approach are improved relative to conventional MP2 theory. Furthermore, with this modified form of the MP2 energy, it is possible to evaluate the energy with only 4^{th} order work, without cutoffs, in contrast to the usual 5^{th} order scaling. We report chemical results and timings.

Third, as time and progress permit, we will discuss some new approaches for exploiting localized orbitals to further accelerate the computation of electron correlation energies.

Towards the Incorporation of Higher-Order Excitations into Time-Dependent Density-Functional Theory

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The grand majority of applications of time-dependent density-functional theory (TDDFT) for the calculation of electronic excitation spectra use the adiabatic approximation and the formalism described in Ref. [1]. It was already pointed out in that reference that the adiabatic approximation restricts the formalism to treating only one-electron excitations, even though configuration interaction (CI) is explicit for one-electron excitations and even though higher-order correlations are included implicitly via the exchange-correlation functional. Nevertheless, it is necessary to include two-electron (and perhaps higher-order excitations) explicitly in order to obtain an acceptable description of (i) lower excitation energies in polyenes, (ii) a correct treatment of exictations in open-shell molecules, and (iii) excitations in molecules when the single determinant description of the ground state is insufficient. I will discuss one or more of these problems and I will give some suggestions for a more general theory.

[1] M.E. Casida, in *Recent Advances in Density Functional Methods, Part I*, edited by D.P. Chong (World Scientific : Singapore, 1995), p. 155. "Time-dependent density-functional response theory for molecules"

Potential hypersurfaces and quantum dynamics of chiral molecules without and with electroweak parity violation

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The construction of global potential hypersurfaces for the calculation of quantum dynamics of polyatomic molecules is a substantial challenge and our group has contributed in this field for some time, in particular in relation to our research on high resolution molecular spectroscopy, infrared multiphoton excitation and intramolecular kinetics [1–8], which are all usually dealt with on the basis of a parity conserving theory. A fundamentally new aspect arises from introducing the parity violating electroweak nuclear force into the quantum dynamics of chiral molecules, thus generating the new "electroweak quantum chemistry" and electroweak quantum chemical kinetics [9–16]. This field has received considerable new momentum after our theoretical discovery, about a decade ago, that the parity violating energy differences between enantiomers of chiral molecules are predicted to be one to two orders of magnitude larger than previously anticipated [9]. In the lecture we shall first report about the fundamental aspects and recent history of the field and then discuss the most recent results from our research group in Zürich.

1.Spectra and dynamics of coupled vibrations in polyatomic molecules, M. Quack, Annu. Rev. Phys. Chem. **41**, 839-874 (1990)
2.Potential energy surfaces, quasiadiabatic channels, and intramolecular dynamics of $(HF)_2$ and its isotopomers, M. Quack and M. Suhm, J. Chem. Phys. **95**, 28-59 (1991)
3.HF dimer, W. Klopper, M. Quack and M.A. Suhm, J. Chem. Phys. **108**, 10096-10115 (1998)
4.Global analytical potential hypersurfaces for large amplitude nuclear motion and reaction in methane, R. Marquardt and M. Quack, J. Chem. Phys. **109**, 10628-10643 (1998)
5.A new six dimensional analytical potential for the electronic ground state of hydrogen peroxide, B. Kuhn, T.R. Rizzo, D. Luckhaus, M. Quack and M.A. Suhm, J. Chem. Phys. **111**, 2565-2587 (1999)
6.Tunneling dynamics of the NH chromophore in NHD_2 during and after coherent infrared excitation R. Marquardt, M. Quack, I. Thanopulos, and D. Luckhaus, J. Chem. Phys. **118**, 643-658 (2003)
7.Global analytical potential hypersurface for large amplitude nuclear motion and reactions in methane. II. R. Marquardt, M. Quack, J. Phys. Chem. **108**, 3166–3181 (2004)
8.Molecular spectra, reaction dynamics, symmetries and life, M. Quack, Chimia, **57**, 147–160 (2003)
9.Ab initio calculation of molecular energies including parity violating interactions
A. Bakasov, T.K. Ha and M. Quack, in Proc. of the 4th Trieste Conference (1995), *Chemical Evolution: Physics of the Origin and Evolution of Life*, 287-296, J. Chela-Flores and F. Rolin eds, Kluwer Academic Publ. Dordrecht, 1996
10.Ab initio calculation of molecular energies including parity violating interactions, A. Bakasov, T.K. Ha and M. Quack, J. Chem. Phys. **109**, 7263-7285 (1998)
11.Multi-configuration linear response approach to the calculation of parity violating potentials in polyatomic molecules, R. Berger and M. Quack, J. Chem. Phys. **112**, 3148-3158 (2000)
12.Influence of parity violating weak nuclear potentials on vibrational and rotational frequencies in chiral molecules, M. Quack and J. Stohner, Phys. Rev. Lett. **84**, 3807-3810 (2000)
13.Parity violation in fluorooxirane, R. Berger, M. Quack and J. Stohner,
Angew. Chemie **113**, 1716–1719 (2001); Angew. Chem. Intl. Ed. (Engl.) **40**, 1667–1670 (2001)
14.Mode-selective stereomutation tunneling as compared to parity violation in hydrogen diselenide isotopomers $^{1,2,3}H_2{}^{80}Se_2$, M. Gottselig, M. Quack, and M. Willeke, Israel J. of Chemistry, **43**, 353–363 (2003)
15.Combined multidimensional anharmonic and parity violating effects in CDBrClF
M. Quack and J. Stohner, J. Chem. Phys. **119**, 11228 – 11240 (2003)
16.Mode-selective stereomutation tunneling and parity violation in $HOClH^+$ and H_2Te_2 isotopomers, M. Gottselig, M. Quack, J. Stohner, M. Willeke, Int. J. Mass Spectrometry **233**, 373–384 (2004)

Quantum Dynamics at High Excitations: From Vibrations to Reactions

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In the limit of sufficiently high excitation energies even semi-rigid vibrations undergo very large amplitudes eventually leading to chemical reactions. Such processes range from conformational changes to the rearrangement of chemical bonds even in the case of strictly bound-state dynamics.

This contribution discusses a general approach to the theoretical description of such processes with particular emphasis on the concept of vibrational adiabaticity. Beyond purely numerical aspects this includes the systematic development of approximate models to describe the dynamical characteristics associated with certain structural features.

The approach builds on a generalized coordinate treatment of multi-dimensional quantum dynamics, recently extended to multi-arrangement quantum dynamics, which encompasses the exact treatment of four-particle dynamics in 6D as a special case. Examples will include the stereomutation tunneling in hydrogen peroxide close to dissociation as well as the cis-trans isomerization and (1,3)-Hydrogen transfer in nitrous acid.

Two problems in the theory of open quantum systems: adiabatic dynamics, and a post-Markovian master equation

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The theory of open quantum systems deals with systems coupled to an external, uncontrollable environment. One attempts to deduce a reduced dynamical description for the system alone. In this talk I will report on the solution of two problems in the theory of open systems:

1. The generalization of the adiabatic theorem of closed quantum systems to the general open systems case (Reference: http://xxx.lanl.gov/abs/quant-ph/0404147).

2. The derivation of a master equation for the system density matrix that explicitly includes bath-memory effects ("post-Markovian"), is analytically and numerically tractable, and satisfies the formally important condition known as complete positivity (Reference: http://xxx.lanl.gov/abs/quant-ph/0404077). Both results will be illustrated via examples.

Stochastic Hartree-Fock: new exact methods for electronic structure and vibrational dynamics

Joshua Wilkie

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New general variationally derived methods for solution of the quantum N-body problem are discussed. These approaches are dynamical in nature but can also be used to calculate spectral information. The procedure expresses the N-body wavefunction or density matrix as an ensemble average of appropriately symmetrized Hartree products of one-body wavefunctions or densities which obey stochastic wave equations. The averaged quantities obey the exact N-body Schroedinger or Liouville-von Neumann equations. Decompositions of this type can be applied to fermions, bosons, vibrations or any combination of particles. The principle difficulty limiting application of the method is numerical solution of the stochastic wave equations. Efficient and accurate numerical methods for solving stochastic differential equations have not yet been developed. We explain how Runge-Kutta methods for ordinary differential equations can be modified to solve stochastic differential equations, and develop an adaptive stepsize algorithm. We solve the Schroedinger equation for He to illustrate the approach.

Exploring Potential Energy Surfaces for Chemical Reactions

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Potential energy surfaces form a central concept in the application of electronic structure methods to the study of molecular structures, properties and reactivities. Reaction path following and ab initio molecular dynamics explore larger regions of these potential energy surfaces than can be characterized by optimizing of equilibrium structures and searching for transition states. For reaction path following, a new Hessian based predictor-corrector algorithm with updating will be described and illustrated with a number of examples. Applications of Born-Oppenheimer methods for ab initio molecular dynamics will be discussed for acetylene dication fragmentation and acetone radical cation dissociation. In extended Lagrangian methods for molecular dynamics, the electronic density matrix is propagated along with the nuclear motion. The ADMP method for extended Lagrangian molecular dynamics will be described.

Recent Progress in the Development of Exchange-Correlation Functionals

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This presentation will address our current efforts to develop more accurate exchange-correlation functionals for DFT. The functionals to be discussed include a new meta-GGA denoted TPSS [1], a screened exchange hybrid especially designed with solids in mind [2], local hybrids [3], and a current (**j**) dependent extension of PBE [4]. Extensive benchmarks and applications will also be presented.

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Potential Functionals: Solution to the v-representability Problem and Theoretical Foundation for the Optimized Effective Potential in Density Functional Theory

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We have constructed a functional of external potentials and its variational principle for the ground-state energy. This potential functional formulation is dual to the density functional approach and provides a solution to the v-representability problem in the original Hohenberg-Kohn theory. A second potential functional for Kohn-Sham non-interacting systems establishes the theoretical foundation for the optimized effective potential (OEP) approach and results in efficient approaches for ensemble Kohn-Sham calculations.

We have developed efficient methods for OEP calculations, based on direct optimization in the potential functional space. Calculations with exact exchange and with exact exchange plus correlation will be presented.

I will present a direct optimization method for the computation of the Kohn-Sham kinetic energy functional, the exchange-correlation potential and other density functionals including the exchange-correlation energy from a given electron density. The method is based on the construction of variational functionals of the one-electron potential. Application to excited state TDDFT calculations will be described.

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Reaction volume Hamiltonian for molecules with large amplitude internal motions

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An analysis of the differential equations obtained by the requirement of vanishing normal coordinate forces in the nonrigid rotation–large amplitude internal motion (LAM) Hamiltonian operator of a molecule with one or more ($L \geq 1$) LAMs is carried out with the following result. The reaction path equation introduced by Fukui and the corresponding zero order rotational-LAM Hamiltonian operator are rederived and generalized to several dimension, i.e. to reaction surface (L=2) , reaction volume (L=3), and reaction hypervolume (L>3) equations and Hamiltonians.

A spectroscopic potential energy surface for the water dimer $(H_2O)_2$

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We report progresses on elaborating a Potential Energy Surface (PES) for the water dimer $(H_2O)_2$, including all the degrees of freedom. Such a PES is required in order to assess the role of the water dimer in the solar absorption spectrum, as well as in the millimeter wavelength domain (radiotelescope arrays).

This surface is to be fit to experimental data, such as the far- and mid-infrared transitions, and the IR shifts obtained in molecular beams. The water dimer is described in its full dimensionality by collision type coordinates in order to access the whole configuration sampled by this floppy system. Internal motions of the monomers (stretches and bends) are explicitly considered by invoking an adiabatic separation between the slow (intermonomeric) and fast (intramonomeric) modes. This (6 + 6)*d* adiabatic formulation allows us to recast the calculations into an equivalent six-dimensional problem (~ pseudo-rigid monomers) on an *effective* potential energy surface. A modified MCY potential was then fitted to a fully flexible dimer potential, which leads to very good agreement with all far- and mid-infrared frequencies (rms ~ 1.5 cm^{-1}). It is shown that flexibility is essential in order to reproduce the experimental transitions. Finally, we describe an attempt at improving our model by adjunction of an anisotropic polarizability component. .

Computational Thermochemistry and Thermochemical Kinetics

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Our research group is studying a number of areas of computational thermochemistry and thermochemical kinetics. My lecture will include several topics drawn from this collection of research projects, which includes:

Density functional parametrizations and density functional validations. The functionals include hybrid DFT optimized for kinetics (MPW1K), hybrid meta DFT optimized for kinetics (BB1K, MPWB1K), doubly hybrid DFT (MC3MPW), and doubly hybrid meta DFT (MC3BB), where MC3 methods are based on combining MP2 with scaling and DFT (as compared to hybrid DFT that is based on combining Hartree-Fock and DFT). The validation suites include bond energies of organic, metal dimer, and organometallic species, energies of reaction, barrier heights and transition state geometries, ionization potentials, electron affinities, vibrational frequencies, hydrogen bonding energies and geometries, weak interaction energies, and equilibrium distances in van der Waals dimers. Coworkers: Yan Zhao, Nate Schulz, Ben Lynch.

Multi-coefficient correlation methods (MCCMs), including SAC/3, MC-QCISD/3, MCG3/3, and BMC-QCISD. The balanced multi-coefficient (BMC) method is based on a new basis set, 6-31+B(d,p) that is the same size as 6-31+G(d,p) but better balanced; this basis set also provides better performance with single-level methods and hybrid DFT. Coworker: Ben Lynch.

A new universal solvation model, SM5.43R, parameterized for Hartree-Fock, DFT, and hybrid DFT with any fraction of Hartree-Fock exchange. It is based on class IV charges obtained by Charge Model 3 (CM3) with redistributed Löwdin population analysis, the generalized Born model, and atomic surface tensions; it has very stable analytic gradients and no outlying charge error. It yields an improved potential of mean force for hydrophobic interactions. As compared to the C-PCM, D-PCM, and IEF-PCM models in *Gaussian 03*, the mean errors for aqueous solvation energies of ions are a factor of 1.3 to 2.2 smaller (depending on the PCM method), and those for neutrals in water are a factor 1.5 to 2.4 smaller than PCM. *Gaussian 03* supports 16 organic solvents, and the PCM methods have mean unsigned errors of 3.8 to 3.9 kcal/mol in these, whereas SM5.43R has a mean unsigned error of 0.56 kcal/mol (a factor of 6.7 to 7.0 improvement). Furthermore, the new model was also tested in 60 other solvents with a mean unsigned error of 0.54 kcal/mol. Coworkers: Jason Thompson, Chris Cramer.

New tools for the study of the free energy and dynamics of Al nanoparticles. These include: a new many-body tight binding method, a new effective core potential and valence basis set for DFT studies, and embedded-atom-type potentials parametrized for Al nanoparticles (Al_{40}-Al_{177}). Coworkers: Nate Schultz, Ahren Jasper, Grazyna Staszewska, and Przemek Staszewski.

Use of hierarchical vibrational configuration interaction to calculate vibrational-rotational energies. We used vibrational CI to calculate a converged vibrational-rotational partition function for CH_4, the first such converged partition function for a molecule with more than three atoms. Coworkers: Arindam Chakraborty, Joel Bowman, and Stuart Carter.

A new Monte Carlo importance sampling scheme for Feynman path integral calculations of absolute vibrational-rotational free energies for molecules with large-amplitude motions. The method employs enhanced same-path extrapolation of trapezoidal Trotter Fourier path integrals and has been used to calculate converged partition functions for H_2O_2, the first converged partition function for a molecule with a torsion. Coworkers: Vanessa Audette Lynch and Steve Mielke.

Time will not permit discussion of all these topics in the lecture, but I will be available for discussion during the entire conference. This work was supported in part by the U. S. Department of Energy, the National Science Foundation, and the Army Research Office.

New Approaches in the Calculation of Magnetic Resonance Parameters

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Recent developments and applications of quantum chemical methods for the calculation of magnetic resonance parameters are discussed. Some of the progress made encompasses
a) improved DFT calculation of magnetic linear response properties (in particular NMR shieldings [1] and EPR g-tensors [2]) using recently introduced "local hybrid potentials",
b) calculation of hyperfine tensors on heavy nuclei using the Douglas-Kroll-Hess Hamiltonian [3],
c) efficient inclusion of spin-orbit corrections into calculations of hyperfine tensors [4], and
d) inclusion of molecular dynamics into electronic g-tensor calculations in solution [5].

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Orbital-dependent functionals: Hartree-Fock, Kohn-Sham exact-exchange and beyond.

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After the local-density approximation and the very successful generalized gradient approximations, it is often stated that using an exact exchange (EXX) functional is the next step up our ladder of DFT approximations. It would notably solve the self-interaction problem that plagues DFT. It only leaves the much smaller correlation energy to be treated with some approximate functional.

We will argue that the EXX approach cannot be considered a step forward compared to the GGAs. It reintroduces a very important flaw present in the Hartree-Fock approximation. Arguably the great success of DFT is a consequence of avoiding the typical Hartree-Fock error, obviating the distinction between exchange and correlation that is so ingrained in quantum chemistry after decades of the reigning paradigm: first Hartree-Fock, and then beyond. We will argue that, once one is prepared to accept the computational complications and the price of dealing with orbital-dependent functionals, it is still not necessary, and maybe even against the origin of the success of DFT, to go back to the exact-exchange starting point. It is possible to go back to the statistical definition of correlation in terms of two-electron probability distributions, or exchange and correlation holes,[1] treating exchange and correlation jointly rather than separately, and devise orbital-dependent functionals that incorporate exchange and correlation on equal footing.[2,3] We will demonstrate that this can be done successfully, but a "universal" functional of this type is not yet available. If such full exchange-correlation functionals will be successful, they may ultimately justify the increased computational expense of dealing with orbital-dependent functionals.

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Local Control Theory for Unitary Transformations: Application to Quantum Computing Without Leakage

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We present a local optimal control strategy to produce desired unitary transformations. Unitary transformations are central to all quantum computational algorithms. Many realizations of quantum computation use a submanifold of states, comprising the quantum register, coupled by an external driving field to a collection of additional mediating excited states. Previous attempts to apply control theory to induce unitary transformations on the quantum register, while successful, produced pulses that drive the population out of the computational register at intermediate times. Leakage of population from the register is undesirable since often the states outside the register are prone to decay and decoherence, and populating them causes a decrease in the final fidelity. In this work we devise a local optimal control method for achieving target unitary transformations on a quantum register, while avoiding intermediate leakage out of the computational submanifold. The technique exploits a phase locking of the field to the system such as to eliminate the undesirable excitation. This method is then applied to produce an SU(6) Fourier transform on the vibrational levels of the ground electronic state of the Na_2 molecule. The emerging mechanism uses two photon resonances to create a transformation on the quantum register while blocking one photon resonances to excited states.

Electronic Structure Studies of Materials Chemistry using Embedded Cluster Models

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In this talk, we consider salient features of mechanical as well as electronic embedding techniques and discuss their applicability in computational studies of materials. Accurate quantum chemical calculations using such embedded cluster models have been performed to investigate the surface chemistry of semiconductor materials and the endohedral chemistry of carbon nanotubes. Recent examples using our results to provide assignments and novel interpretations of experimental spectroscopic observations will be discussed.

Generalizations of the Hohenberg-Kohn Theorems and the *N*-representability Problem

Paul W. Ayers

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Computational theories based on the electron density satisfy the variational principle (the second Hohenberg-Kohn theorem) because the *N*-representability conditions for the electron density are easily enforced. Unfortunately, we do not know the expressions for the electronic energy in terms of the electron density. Using the first-order reduced density matrix, instead of the electron density, as the fundamental descriptor helps (we can construct the kinetic energy exactly), but developing accurate correlation energy functionals still seems difficult. This suggests that the next step—using higher-order density-matrices or many-electron densities—might be helpful. Indeed, constructing energy functionals is easier in these cases. But unlike the electron density and the first-order density matrix, the *N*-representability conditions are no longer easily enforced. This is problematic, since in a straightforward variational procedure, one minimizes the energy with respect to the density matrix *subject to the constraint that the density matrix is N-representable.* Symbolically,

$$E_{g.s.} \leq \min_{\Gamma \text{ in } N} E_v[\Gamma] ,$$

which is just the second Hohenberg-Kohn theorem, with the density matrix replacing the electron density as the fundamental descriptor of the electronic system.

Since non-*N*-representable density-matrices are manifestly nonphysical, one can define their energy however one pleases. By using this freedom, one obviates the need to restrict the variational principle to *N*-representable densities. A simple method for constructing this energy functional will be presented. This represents an "implicit" method for solving the *N*-representability problem, since the *N*-representability constraint is implicit in the functional.

Since there has been some recent interest in theories based on the two-electron (electron pair) density, this talk will conclude by considering the N-representability conditions for these quantities.

Equilibrium, Detailed Balance and "Forbidden hops" in mixed quantum-classical dynamics

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Mixed quantum-classical procedures have been developed to simulate molecular motions when a classical mechanical description alone is not adequate. A crucial property of such theories is feedback between the classical and quantum motions. Quantum transitions are driven by the time-dependent classical motion and, in turn, the forces governing the classical paths are altered by quantum transitions. A desired property of such theories is satisfying detailed balance, required to achieve the correct equilibrium state. It has been widely assumed that mixed quantum-classical theories cannot satisfy detailed balance; rather, quantum populations are believed to approach infinite temperature. We examine the two general formalisms that have evolved for incorporating quantum-classical feedback, the self-consistent-field (SCF) and surface-hopping methods. We present an analysis of detailed balancing in these methods, supplemented by simulations. We show that with the SCF method the quantum populations are generally much higher than the desired Boltzmann values, and indeed can approach infinite temperature at long times. By contrast, surface hopping with the "fewest switches" algorithm usually satisfies detailed balance quite accurately, albeit not exactly. This is only true, however, when transitions to energy forbidden quantum states are disallowed. Thus "forbidden hops", often considered a failing of surface hopping, are actually essential to achieve proper equilibrium.

Quantum Dynamics of Reactant Channel OH-CO Complexes

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The results of a six-dimensional wave packet simulation of the decay of OH-CO reactant channel complexes are discussed. These complexes have been studied experimentally in recent work by Lester and co-workers. The theoretical work presented here employs recently developed potential energy surfaces based on high quality *ab initio* data for the complexes. Both the A' and A" surfaces are considered. Excitation of the overtone with two quanta of excitation in the OH vibration leads to very long-lived complexes that decay exclusively to separated OH and CO fragments. The product distributions reflect two mechanistic pathways, one involving direct fragmentation after loss of one quantum of vibration in OH, and the other pathway reflecting a simultaneous vibrational excitation of the CO fragments. Our results are found to be in good accord with the experimental ones. Preliminary results on the decay of excited bend states of the reactant channel complexes, which can also decay through more chemically-bonded HOCO complexes and lead to H+CO_2 products, are also presented.

This work was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, U. S. Department of Energy under Contract No. W-31-109-ENG-38.

Ab initio potential surfaces and vibrational calculations for 4-7 atom molecules

Joel M. Bowman,[1] Bastiaan Braams,[2] Alex Brown,[1,3] Stuart Carter,[1,4] Hua Guo,[5] Lawrence Harding,[6] Xinchuan Huang,[1] Anne McCoy,[7] Xiubin Zhang,[1] Shengli Zou[1,8]

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I will describe progress we have made in obtaining global or semi-global potential energy surfaces for polyatomic molecules and a variety of dynamics calculations done with these potentials. Examples will include acetylene/vinylidene isomerization, CH_5^+, $(OH^-)H_2O$, H_2CO, $(H_2O)_2$, and $H^+(H_2O)_2$.

Support from the National Science Foundation, Department of Energy and Office of Naval Research is gratefully acknowledged.

Density functional theory for the calculation of the molecular conductance

Matthias Ernzerhof

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Stationary current transport through molecular electronic devices represents a non-equilibrium problem. We develop a non-hermitian model Hamiltonian that yields eigenstates describing the non-equilibrium state. A stationarity principle for the non-hermitian Hamiltonian is constructed that resembles the variational method of conventional hermitian quantum mechanics. As an application of the non-hermitian stationarity principle, we develop a density functional theory for the current-carrying state in molecular electronic devices. We obtain a non-interacting model system that yields the same current density as the interacting one.

Reconciling Semiclassical and Bohmian Mechanics

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Semiclassical and Bohmian mechanics share many similarities. Both are trajectory methods, that can capture quantum mechanical effects such as interference. Both are derived from the notion of the action, and the Hamilton-Jacobi equation. Both utilize the same modulus-phase decomposition of the wavefunction. Yet dynamically, the two approaches are radically different, e.g. the quantum potential is not "small" in any hbar sense, and the trajectories themselves are not even qualitatively similar. In this talk, we reformulate Bohm's theory in a manner that more closely resembles the semiclassical approach, and that also alleviates the infamous "node problem."

Quantum solvation and rotational dynamics in helium clusters

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We describe quantum Monte Carlo approaches for the study of quantum solvation and rotational dynamics in doped helium clusters. Simulation results for a dopant molecule (eg: OCS, N_2O) imbedded in helium clusters of varying sizes will be presented. The solvation structure will be analyzed as a function of system size. Dynamical properties such as the rotational constant of an effective rotor will also be presented. Questions regarding decoupling and the inclusion of particle exchange will be discussed in terms of the onset of microscopic superfluidity. It will be shown that exchange effects appear to be quenched for small clusters and become important when a certain cluster size is reached. This cluster size coincides with the experimentally observed "turnaround" in the behaviour of the effective rotational constant. These observations should help further our understanding of the transition from the cluster to the nano-droplet regime.

Quantum Statistical Mechanics with Gaussians

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The variational Gaussian wavepacket method for computation of equilibrium density matrices of quantum many-body systems is presented.

The density matrix is expressed in terms of Gaussian resolution, in which each Gaussian is propagated independently in imaginary time t=1/kT starting at the classical limit t=0. For a N-particle system a Gaussian is represented by its center, a real 3N-vector, the width, real symmetric 3N×3N matrix, and the scale, a real number, all treated as dynamical variables. Evaluation of observables is done by Monte Carlo sampling of the initial Gaussian positions.

Ideally, a single Gaussian propagation requires numerical effort comparable to propagation of a single classical trajectory for a system with 9N(N+1)/2 degrees of freedom. Furthermore, an approximation based on a direct product of single-particle Gaussians, rather than a fully coupled Gaussian, reduces the number of dynamical variables to 9N.

The success of the methodology depends on whether various Gaussian integrals needed for calculation of, e.g, the potential matrix elements or pair correlation functions could be evaluated efficiently. I will describe techniques to accomplish these goals.

At not-very-low-temperatures the results are surprisingly accurate for a range of model systems including the case of double-well potential. The method was also applied to a Ne_{13} Lennard-Jones cluster to compute the heat capacity and radial pair correlation function. The results agree very well with the available Path-Integral-Monte-Carlo calculations.

I will also discuss how symmetrized Gaussians can be used to include particle statistics and the numerical difficulties associated with it.

Contributed Posters

Ordered alphabetically by presenting author

A Density Functional study for paracetamol and 3,5-disubstituted analogues

J. E. M. Diniz, R. S. Borges, and C. N. Alves

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Quantum chemistry calculations at the B3LYP theory level, together with the 6-31G* basis set were employed to obtain energy (E), ionization potential (IP), bond dissociation energies (BDE), and spin-density distribution for paracetamol (PAR) and 3,5-disubstituted analogues of PAR. Calculations of spin densities were performed for radical formed by hydrogen abstraction from the phenolic hydroxyl group. The unpaired electron remains is localized on the O_7 phenolic oxygen (31-40%), C_3 and C_5 carbon atoms at the *ortho* (17-27% and 21-27%) and C_1 carbon atom at the *para* (25-33%) positions. The correlation between analgesic activity, cytotoxicity, and electronic properties was obtained by using correlation matrix. The IP and BDE_{O-H} are significant related with the *in vitro* inhibition of cyclooxygenase, while BDE_{O-H}, BDE_{N-H} and IP are significant related with the cytotoxicity (LDH).

Keywords: *paracetamol analogues, analgesic activity, cytotoxicity, DFT, spin density.*

A Density Functional study of dipyridamole

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A DFT study of charge distributions for dipyridamole in the neutral, single- and double-ionized states allowed to estimate the first and second ionization potentials. Results are compared with electrochemical oxidation, a sequential two-step process. Single ionization produces a cation radical, the electron being removed from the nitrogen atoms in the substituent positions 2,4,6,8 with participation of the carbons in the pyrimido-pyrimidine ring. Protonation of one of the nitrogens is allowed energetically while a second protonation is forbidden due to the high energy required. Our calculations allow to explain some interesting experimental results related to electrochemical oxidation and protonation of the drug.

Poster Session A, Monday afternoon

Photodissociation of HI and DI: Atomic photofragment polarization

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The complete angular momentum distributions and vector correlation coefficients (orientation and alignment) of ground state $I(^2P_{3/2})$ and excited state $I(^2P_{1/2})$ atoms resulting from the photodissociation of HI have been computed as a function of photolysis energy. The orientation and alignment parameters, $\mathbf{a}_Q^{(K)}(p)$, that describe the coherent and incoherent contributions to the angular momentum distributions from the multiple electronic states accessed by parallel and perpendicular transitions, are determined using a time-dependent wave packet treatment of the dissociation dynamics. The dynamics are based on potential energy curves and dipole moments that have been reported previously [R.J. Le Roy, G.T. Kraemer and S. Manzhos, *Journal of Chemical Physics* **117**, 9353-9369 (2002)] and used to successfully model the scalar (cross-section and branching ratios) and lowest order vector (anisotropy parameter β) properties of the photodissociation. Predictions of the $\mathbf{a}_Q^{(K)}(p)$ parameters for the isotopically substituted species DI are reported and contrasted to the analogous HI results. Comparison of these predictions for HI and DI with experimental measurement will provide the most stringent test of the current interpretation of the dissociation based on non-coupled excited state dynamics.

Non-Born-Oppenheimer Quantum Chemistry

Mauricio Cafiero

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Quantum chemistry, and especially computational quantum chemistry, has traditionally been done within the Born-Oppenheimer approximation. Occasionally, when the circumstances demand it, the Born-Oppenhemier corrections are added to conventional calculations to take into account the coupling of electronic and nuclear motion. The separation of electronic and nuclear motion (and thus the perturbative correction to correct for it) is accurate only to second order, so any effects which are inherently above second order cannot be described within the Born-Oppenheimer picture. As experimental techniques allow us to examine molecular behavior in these regimes with increasing accuracy, it is nessesary that we develop the computational and interpretive tools to examine the experimental results. We present some results of the non-Born-Oppenheimer calculations we have been doing for the last several years and discuss some of the conceptual consequences of not invoking this approximation (for example, the disappearance of molecular structure).

A Correlation Scheme for use with Exact Exchange Functionals in DFT

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Conventional DFT correlation functionals have been shown to be incompatible with exact exchange (that is, Hartree-Fock exchange). We present a simple scheme for modifying any given combination of GGA DFT eXchange/Correlation functionals which recovers exact exchange behavior and yields total XC energies at least as accurate as conventional GGA's in the calculationof themochemical properties. The modification of GGA correlation functionals used here is shown to be a self-consistant generalization of Becke's Correlation Scheme in his Hybrid: B3PW91. Properties calculated include atomization energies, ionization potentials, electron affinities, and total energies.

Theoretical Study of Spin-Crossover in Model Ferrous Compounds: Comparison of DFT and *Ab Initio* Methods for Describing the Singlet and Quintet States of $[Fe(H_2O)_6]^{2+}$ and $[Fe(NH_3)_6]^{2+}$

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Université Joseph Fourier, Grenoble, FRANCE
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Octahedral ferrous complexes can exist in both high-spin [HS : $(t_{2g})^4(e_g)^2$] and low-spin (LS: $(t_{2g})^6(e_g)^0$] states. The two states have different magnetic properties and, not infrequently, different colors. The transition from one state to the other can be induced thermally, by pressure, or by light, all of which have interesting potential consequences for displays and storage devices. Our particular ultimate interest is in light-induced excited spin-state trapping (LIESST [1]). Typical HS-LS separations in LIESST compounds are on the order of 100 cm^{-1} – 1000 cm^{-1}, offering a substantial challenge for any quantum chemical method, though the size and presence of a 3d transition metal in typical LIESST compounds would seem to make DFT the method of choice. We have assessed different functionals for their ability to give meaningful HS-LS energy differences for $[Fe(H_2O)_6]^{2+}$ and $[Fe(NH_3)_6]^{2+}$. We find that the LDA overstabilizes the LS state compared to the HS state ("the DFT pairing energy problem") and this tendancy is often inherited by different GGAs. However some modern functionals seem to be relatively free of the DFT pairing-energy problem. Some of our results have been published [2] while others will soon be submitted [3].

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An AIM Characterization of the Neutral, Cationic and Anionic Forms of trans- and cis-$C_{10}H_{12}$.

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The synthesis of new conducting polymers has been shown to be an exciting area in chemistry after the first report of conducting organic materials by Heeger, MacDiarmid and Shirakawa in 1997 for which they were awarded the Nobel Prize in Chemistry in 2000. The first studies on conducting organic materials were carried out on polyacetylene. The *trans* and *cis* forms of polyacetylene are semiconductor materials but when electrons are removed or inserted into them, their conductivity increases by orders of magnitude. This paper reports an AIM study based on the negative divergence of the quantum stress tensor of the neutral, cationic and anionic forms of *trans*- and *cis*-$C_{10}H_{12}$, in an effort to shed light on the electronic origin of the conductivity. The effect of an electric field on all systems is also analyzed in terms of AIM parameters. Hydrogen-hydrogen bonds were found in the *cis* polyacetylene systems and their characterizations are reported.

A Multidimensional discrete variable representation basis obtained by simultaneous diagonalization

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Multidimensional DVR bases are usually constructed as a direct product of 1D DVRs. Although restrictive and inefficient (large numbers of functions are required), direct product bases are advantageous computationally. In particular, the coordinate operator is diagonal, leading to trivial evaluation of the potential energy contribution to Hamiltonian matrix-vector products. We discuss how an efficient (smaller) non-product basis may be constructed in two or more dimensions retaining maximal diagonality of the coordinate representations, and thus a potential that is approximately diagonal. Eigenvalues are then computed using this approximation. The effectiveness of this method is evaluated for some model 4D problems using two dimensions for each contraction. Results will be discussed for stretch type problems such as coupled Morse oscillators and skewed multi-well potentials, as well as for bend problems using a basis of spherical harmonic functions. The success of this approach could allow theorists to compute the spectra, rate constants etc, for systems beyond the reach of conventional methods.

Computational Modeling of Processes Leading to Self-Directed Assembly on Silicon Surfaces: Progress Toward Hybrid Organic-Silicon Nanostructure Formation

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We anticipate that hybrid organic-silicon nanostructures will underpin a new generation of devices with enhanced functionality. In previous work,[1] we have demonstrated that styrene molecules can undergo a self-directed, radical mediated growth process on hydrogen-terminated Si(100) surfaces. The resulting molecular assemblies are covalently bound to the surface. Nanostructure growth is initiated at predefined points and the extent of growth is controlled. We have since refined our techniques for nanostructure formation with the help of computational chemistry.[2] In this presentation, I will review our recent efforts and highlight the role that theory has played and will continue to play in our progress toward controlled nanostructure formation on silicon surfaces.

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Superconvergent perturbation treatment of non-adiabatic transports of Floquet states in the low-frequency limit.

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In a new formulation of Floquet theory (Jauslin, Guérin, Adv. Chem. Phys....), the quasi-static picture emerges as the zero-frequency limit of the Floquet representation. For low, but finite, non-zero frequency, non-adiabatic corrections to this zero-frequency Floquet representation can be obtained by applying superconvergent perturbation techniques, yielding rapidly sucessive higher-order adiabatic Floquet representations. We illustrate the procedure on two classes of time-dependent, laser-driven systems, namely harmonic oscillators and two-level systems.

Decoherence in an Anharmonic Oscillator Coupled to a Thermal Environment: A Semiclassical Forward-Backward Approach

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The decoherence of an anharmonic oscillator in a thermal harmonic bath is examined via a semiclassical approach. A new computational strategy is presented and exploited to calculate the time dependence of the purity and the decay of individual matrix elements in the energy representation for a variety of initial states. The time dependence of the decoherence is found to depend on the temperature of the bath, the coupling strength, the initial state of the oscillator, and the choice of quantity measuring the decoherence. Recurrences in the purity and in the off-diagonal matrix elements are observed, as well as the collapse of these matrix elements to the diagonal, providing evidence for the retention of quantum coherence for time scales longer than that indicated by the purity. The results are used to analyze the utility of the Caldeira-Leggett and Redfield models of decoherence and to assess the dependence of dephasing rates on the degree of structure in phase space. In several cases we find that the dephasing dynamics can be described as an initial Zeno-effect regime, followed by a Caldeira-Leggett region, followed by recurrences.

Reaction Path at room temperature: Calculating the Free Energy Gradient

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The free energy profile of a reaction can be estimated in Molecular Dynamic (MD) approach by imposing a mechanical constraint along a reaction constraint (rc). Many recent studies have shown that the temperature can greatly influence the path followed by the reactants. Here, we propose a practical way to construct the reaction path directly on the free energy surface (FES) at a given temperature. First, we follow the blue-moon ensemble method to derive the expression of the free energy derivatives for a given RC. These derivatives are then used to find the actual reaction path at finite temperature, in a way similar to the Intrinsic Reaction Path of Fukui. Once this is known, one can calculate the free energy profile using thermodynamic integration. We also show that the mass-metric correction cancels for many type of constraints, making the procedure easy to use. Last, the path at 0 K and 300 K for the reaction: ethene + dichlorocarbene → 1,2-dichloro-cyclopropane

Global Optimization by Tabu Search in Descriptor Space

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Many problems are formulated as global optimization of functions of many variables, for example, predicting the structures of peptides or clusters, or drug design by maximizing scoring functions. We devised a global optimization method called "Tabu Search in Descriptor Space" (TSDS). It has certain features that distinguish it from most other optimization methods, like simulated annealing (SA) and genetic algorithms (GA), and that make it especially suitable for optimization of functions that are costly to evaluate, such as Kohn-Sham (KS) potential energy surfaces. Test optimization runs on Lennard-Jones cluster geometries show that TSDS requires ten to a hundred fewer energy evaluations to locate global energy minima than one of the best variants of GA. This efficiency comes from three things:

1) TSDS implicitly simplifies the function by mapping all points in the variable space onto a discrete subset of points (this is similar to "basin hopping"), and then mapping those points onto a descriptor space that has fewer dimensions than the original variable space;
2) one can incorporate expert knowledge into TSDS without biasing the search;
3) TSDS uses all the information accumulated about the function since the beginning of the search, not only information obtained in the last few steps.

The main drawbacks of TSDS are that: (a) the methods are not easily transferred from one type of optimization problem to another (ie, optimizing the structure of peptides instead of clusters requires substantial new computer code); (b) it requires at least a little "a priori" knowledge about the function to be optimized; (c) it is truly efficient only when the computational cost for one function evaluation is high (on the order of 100 million FLOPS or more, roughly). We will show results of calculations where TSDS was combined to KS theory to study the structure of clusters of Li, Be, Al, and Si, and discuss potential applications of TSDS/KS to other systems.

A Bohmian total potential view to dynamics: quantum effects go classical

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The coherent-state wave packet dynamics of several model systems is analyzed in terms of Bohm´s total potential. The quantum dynamics has been obtained by solving the time-dependent Schrödinger equation, and a method for obtaining the total potential from it, involving just matrix algebra, has been proposed. Contrary to what one may expect, it is shown that the time- and state-dependent features of the total potential admit a rationale, classical-like description of quantum effects, leading to a unified picture, which is not critically dependent, as for the key features, on the classical potential.

An outstanding feature is found to be the relation of the state system's density amplitude and sharpness (in its dependence with position) whit quantum effects. Sharp density profiles and low densities cause the total potential to strongly depart from the classical value, in both time regimes and position ranges, which provide a clearer, more deterministic view to quantum dynamics. Free motion, as well as scattering processes by square and Eckart barriers, have been analyzed by means of careful inspection of several time dependent snapshots, providing an insightful picture of processes involving tunneling and antitunneling, including their dynamical variant, as well as resonances and quantization.[1]

Another relevant fact is the possibility of tracking the time–development of quantum effects. For instance, it has been obtained that the total potential, as originated by a free gaussian wavepacket, dominates an important fraction of the collision event. Even when the packet is traversing the classical potential barrier, and thus being strongly distorted from its original gaussian shape, the total potential is strongly reminiscent of the free packet. This feature prompts an interesting effect: since a free packet spreads as it travels towards the classical barrier, and since the total potential is dominated by the effect of the free packet, one should obtain a *quantum transmission dependent on the initial distance between the packet and the barrier*. This should be so, for quantum effects are triggered by the total potential shape, and the latter depends on the degree of spreading of the free packet. This type of quantum effect, amenable of being experimentally tested, has been checked numerically, for both square and Eckart one–dimensional classical barriers. It has been found that, under the proper barrier dimensions and packet mean energies, the quantum transmission may vary, as a function of the initial launching distance of the packet, up to 20% per Ångstrom.[2]

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How do inert gas atoms affect molecular properties?.

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Despite inert gases being usually quite 'inert', they may strongly affect molecular properties. For example, in AlO the perpendicular component of the electron paramagnetic resonance g-shift Δg ($\Delta g = g - g_e$) has been observed to be -1900 ppm in Ne, -2600 ppm in Ar, and -5000 ppm in Xe matrices (1). The estimated gas-phase value is about -1450 ppm (2). The question is what causes such matrix effects, and why they are especially pronounced in AlO. Since the g-tensor depends mainly on spin-orbit coupling constants, the magnetic dipole moment and excited state energies, one wonders which of these properties are changing, and which are responsible for the matrix effect experienced by AlO and by other radicals.

Using second-order perturbation theory and MRCI wavefunctions (3) with explicit sum-over-states expansions, the perpendicular component of the g-tensor was obtained for AlO surrounded by 2, 4, 6, and 8 Ne or Ar atoms in different orientations and at a series of distances from AlO. Depending on the number and location of the inert gas atoms, the g-shifts may deviate widely from the gas-phase value. In general, but not always, they become more negative, more so for Ar than for Ne, corresponding to the experimental observation.

For comparison, MRCI g-tensor calculations have been performed on the isovalent BO molecule, surrounded by Ne or Ar atoms. Also, comparison will be made with DFT g-tensor results for the same systems.

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Nonadiabatic Dynamics: Surface Hopping Schemes and the Role of Coherence

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Mixed quantum-classical dynamics[1] (MQCD) provides a way of treating nonadiabatic processes, where the Born-Oppenheimer approximation is invalid, in which a small set of quantum degrees of freedom can undergo transitions between adiabatic surfaces as a result of interactions with an environment that can be adequately described by classical mechanics. Systems of this type arise in a variety of processes in the condensed phase or in biomolecular systems, such as proton or electron transfer reactions or vibrational relaxation. Existing approaches to solving these nonadiabatic problems are based on hopping between adiabatic surfaces[2,3,4] and are phenomenological in nature.

Starting from mixed quantum-classical Liouville dynamics a general master equation is derived by application of projection operator techniques. By making a Markovian approximation, the generalized master equation is reduced to a master equation that describes the dynamics of the projected evolution of a density operator, providing a link to surface hopping schemes that involve transitions among adiabatic quantum states. The transition probabilities in this master equation satisfy detailed balance. A description of how quantum coherence and decoherence manifests itself in the quantum subsystem as a result of interactions with the classical environment can also be obtained through an analysis of this generalized master equation formalism.

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Molecular Dynamics Simulation Study of 1,2-Disubstituted (Hydroxy- and Amino-) Ethanes: the Local Structure in Pure Liquids and Their Aqueous Solutions

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This paper is a comparative computational study of the local structure of three widely used representatives of 1,2-disubstituted ethanes, namely ethylene glycol (EG), ethylenediamine (ED) and 2-aminoethanol (AE), in liquid state and their mixtures with water. Classical molecular dynamics combined with three-dimensional atomic density maps, known as spatial distribution functions (SDF's), are the computational tools used in this study.

The present work consists of three parts. In the first part twelve molecular models were designed and gas-phase simulations for each were carried out. The results obtained were compared with the most reliable experimental estimates in order to test different force fields and molecular representations. In the second part liquid-phase simulations were performed on the most successful (AMBER/OPLS-based) models. The heats of vaporization and self-diffusion coefficients were used as criteria for the final selection of molecular models to be employed in the subsequent simulations of aqueous solutions.

In the third part a detailed structural analysis was performed. As an essential part of this analysis the dihedral angle distributions were calculated and relative populations of isomers with respect to the central dihedral angle were determined for pure EG, ED and AE, as well as their mixtures with water, where four compositions of each compound were considered. It has been confirmed that in the liquid phase the *gauche* conformation accounts for the major population of isomers for EG and AE, while ED exhibits a significant population of *trans* conformers. Additionally, the first theoretical estimates of the compositional dependence of self-diffusion coefficients for the aqueous solutions of EG, ED and AE were obtained. The analysis of radial distribution functions in conjunction with calculated numbers of nearest neighbors around oxygen and nitrogen atoms of the main functional groups provided some structural insights into the H-bonding pattern of the systems studied. The number of strongly H-bonded neighboring groups was determined and their possible positions were located by means of SDF's. The possibility of four-membered H-bond arrangements (comprised of two strong and two weak H-bonds) found around oxygen and nitrogen atoms leads to the conclusion that in the liquid phase the generalized H-bonding pattern for EG, ED and AE can be described as a three-dimensional, branched network.

Quantum-classical transition via a generalized momentum operator

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We propose a phenomenological approach to the quantum-classical transition via a generalized momentum operator. This operator contains, in addition to the standard quantum expression, a term which is a functional of the N-particle density. We show that this implementation has a formal relationship with Witten's approach to supersymmetric quantum mechanics via deformation of the exterior derivative.

Quantum-classical dynamics of proton transfer reactions in the condensed phase

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Proton transfer is of great general importance to many processes in chemistry and biology. Studies of proton transfer in the condensed phase require that one consider the dynamics of quantum systems with a large number of degrees of freedom. However, it is not computationally feasible to perform full quantum mechanical simulations of such systems. Therefore, one is led to consider the dynamics of a quantum subsystem coupled to a classical bath. An approach to studying such a composite system is quantum-classical molecular dynamics (QCMD). The main idea is to treat a few crucial degrees of freedom (e.g. proton) quantum mechanically and the rest of the system (e.g. solvent) classically. A simple model for a proton transfer reaction in a linear hydrogen-bonded complex dissolved in a polar liquid solvent will be investigated using QCMD. The rate constant for the adiabatic proton transfer is computed using the reactive flux correlation function.

A closer look at chemical reactivity and reaction mechanisms using DFT-based reactivity indices

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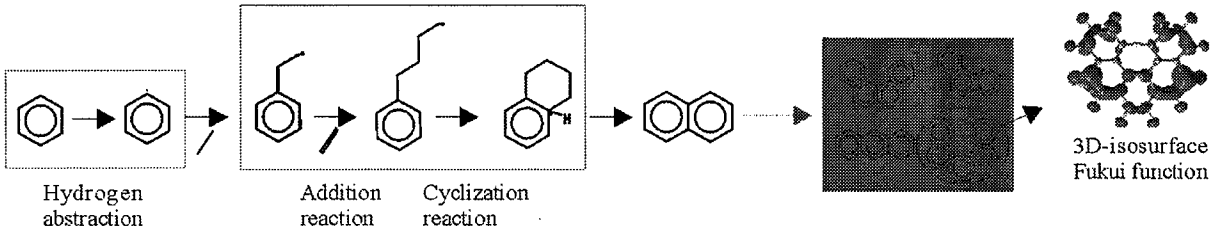
The chemical reactivity of all atomic and molecular systems can be described through different properties, calculated within the Density Functional Theory (DFT) framework [1]. The reactivity of molecular species involved in chemical reactions, is described using information of the reactants only. Various DFT based reactivity indices may provide chemical information at a low computational cost compared to more classical theories (e.g. transition state theory). Consequently, there is a broad area of application. Information about the reactivity of the molecule as a whole is provided by the global descriptors, such as the chemical potential or the hardness. In addition to this information, local indices (Fukui function, local hardness and local softness) are used to assess the problem of site-selectivity during a chemical reaction.



In view of chemical reactions, indicators are validated through the application of some chemical principles such as the hard and soft acids and bases (HSAB) and the maximum hardness (MHP) principle. The first principle (of which a global and local variant can be found) states that the interaction between two species is favored in case of similar softnesses. According to the MHP, molecular systems at equilibrium tend towards states of higher hardness and consequently, the transition state of a reaction should have a minimum hardness value. The latter principles provide knowledge that can be used to assess the importance of competing reaction routes.

In this work, the reactivity of benzene and larger polyaromatic structures, which are important in various fields of hydrocarbon chemistry, is studied using the DFT global indicators [2],[3],[4]. Furthermore, their reactivity in hydrogen abstractions by an approaching methyl radical and additions to double bonds both intra and intermolecular are investigated (Figure). As such, the softness reactivity index is tested on its usefulness and reliability to provide information about the reactivity of the global molecule or about chemical selectivity. The applicability of the HSAB principle for bimolecular radical reactions is illustrated by comparing the results of the softness-matching criterion with kinetic and thermodynamic data. Energy and hardness profiles are provided, testing the applicability of the MHP.

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Semiclassical Dynamics with Constraints

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The Semiclassical Initial Value Representation (SC-IVR) approach offers a means of describing quantum dynamics based on classical trajectories. Motivated by the need to find practical implementation methodologies, a general approach has been developed for the study of rigid molecular systems in cartesian coordinates, based on the SC-IVR. An interesting feature of the technique is that it eliminates the necessity to define a new coordinate system. Generally, the SC-IVR propagator involves an integration over an oscillatory integral. However, freezing out high frequency motion due to stiff chemical bonds through the incorporation of geometrical constraints renders the integrand less oscillatory. As a consequence, the treatment of quantum effects becomes possible for molecular systems of increasing complexity. Various approaches are being considered and implemented in the Molecular Modeling Toolkit (MMTK) [K. Hinsen, J. Comp. Chem. 21, 79 (2000)]. We will present recent findings along with relevant examples of the implementation.

Study of Enzyme-Catalyzed Reactions using Quantum Mechanical/Molecular Mechanics Methods

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Mechanism of enzyme catalyzed reactions is one of the most important subjects of research in biochemistry and biophysics. Many detail of were obtained for mechanism of some enzyme reactions using experimental methods such as x-ray crystallographic methods. Deep understanding the mechanism of these reactions is still need to be studied using theoretical and computational methods to reveal general aspects of the problem. We have used mixed Quantum Mechanical/Molecular Mechanics method to obtain some hint about the Adenosine Deaminase (ADA) enzymatic characteristics in the presence of different inhibitors. Adenosine Deaminase (ADA) is an essential enzyme for the proper functioning of the human body's immune system, catalyzing the deamination of adenosine to inosine.

Separate MM and QM/MM studies were done on the enzyme-substrate complex. In our QM/MM calculations, the active site of enzyme (Zn^{2+} ion, residues His238, Asp295, Glu217,...and the substrate) was selected as the quantum mechanical part. Some new inhibitors for ADA will be suggested.

Quantum and Semiclassical Monte Carlo Calculations of Protonated Methane

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Protonated methane has long been a puzzling problem in electronic structure and dynamics communities. It is generally regarded that the addition of a proton to methane induces strong structural destabilization, as evidenced by three nearly isoenergetic equilibrium structures and an unassignable (as it currently stands) infrared spectrum measured just above the room temperature. We present quantum and semiclassical studies of delocalization effects in the ground vibrational state of CH_5^+ using a global potential energy surface based on the MP2/AVTZ level of theory.

A recently developed signal processing method has been applied to a time evolved Gaussian wavepacket roughly corresponding to the ground vibrational state of protonated methane at time zero. The time evolution of the wavepacket was described by semiclassical initial value representation theory where classical trajectories are used to evaluate the quantum mechanical time evolution operator. Only about 25000 relatively short time trajectories are necessary to yield a well converged eigenvalue of the ground vibrational state. The calculations reveal an unusually large red shift of 448 cm^{-1} from the harmonic zero point level placing the ground state at 10973 cm^{-1}, with a statistical error of 30 cm^{-1}. These results agree remarkably well with full-dimensionality quantum Monte Carlo calculations.

Path integral calculations support the conjecture about a structureless CH_5^+ at room temperature, i.e., there is no indication of isomerization effects at temperatures above 100 K. Although at lower temperatures we observe localization of the H_2 moiety attached to the CH_3 tripod, which becomes even more pronounced in a triply deuterated species.

The study of harmonic and anharmonic motion in biomolecules using the Driven Molecular Dynamics approach

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The driven molecular-dynamics (DMD) method yields frequencies and normal modes without evaluation of the Hessian matrix. The DMD method employs an external, sinusoidal driving term that can be used to scan the spectrum in a continuous wave fashion and determine resonant absorptions, which for weak signals are the normal modes. The molecular motions, induced by driving at resonant frequencies, correspond to the normal mode vibrations. The driving force is applied to all interatomic distances to ensure that all normal modes will be excited.

We validated the method by calculation of the structural and dynamical properties of a small protein, Trp-cage, such as B-factors, root-mean square fluctuations, anisotropies, vibrational entropy, and cross-correlations coefficients. The results are in very good agreement with ones calculated using standard normal–mode analysis method. Thus, the DMD method provides a viable alternative to the standard Hessian-based method and has considerable potential for the study of large systems, where the Hessian–based method is not feasible.

The important advantage of DMD over the Hessian based normal mode analysis is the ability to study the molecular dynamics away from the harmonic region. Mild driving (small driving parameter) is used to extract the normal modes; harder driving can be used to study anharmonic effects. One can rigorously quantify such fundamental phenomena as anharmonic motion and mode coupling which are relevant to studying functional properties of biological macromolecules.

A particularly useful application of anharmonic DMD is simulation of so-called two-dimensional infrared (2D-IR) experiments broadly aimed at studying energy transfer in time and frequency domains. In relation to the infrared spectroscopy, here we use the DMD method with the dipole-driving scheme to simulate 2D-IR experiment. We present the results of a small peptide, dialanine, which exhibits coupling between amide-I frequencies.

Excitation energies of polyethylene by equation of motion coupled-cluster theory

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A computational method to calculate excitation energies of polymers by equation of motion coupled-cluster (EOM-CC) theory was investigated. In this method cyclic boundary condition was applied, in which a polymers is regarded as a cyclic cluster composed of N unit cells. In the first step, Hartree-Fock theory for periodic systems within linear combination of atomic orbitals was applied. In the next, CC and EOM-CC equations were solved as is done in molecules.

In order to perform CC and EOM-CC calculations, transformed two-electron integrals were obtained from Hartree-Fock orbitals. As basis functions in the CC and EOM-CC calculations, canonical Bloch functions or localized Wannier functions are possible choices. In the present work the former was used. For this purpose, full integral transformation of two-electron integrals from atomic orbital basis to Bloch orbital basis was implemented in the developed computational codes.

As a test case, the lowest singlet and the lowest triplet excited states of polyethylene were studied using STO-3G basis set, and their dependence on system size, N (number of unit cells in the cyclic cluster), was investigated. As a result, it was found that the excitation energies for the lowest singlet and triplet states were converged with increasing N. It was also found that the excitation energy of the triplet excited state was converged faster than that of the singlet excited state.

The excitation energies of polyethylene were also studied using oligomer molecules, in which terminal C-C bonds were substituted by hydrogen. The dependence of the excitation energies on system size N was also investigated. The resultant convergence was worse than those obtained by the above periodic calculations.

Quantum Chemical Approach of Corrosion Inhibition: Structure-Activity Correlations of Some Inhibitors Used for Acid Corrosion of Steel

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Computational calculations on some experimentally tested sulfur-containing corrosion inhibitors were carried out to search possible correlation between electron density distribution on sulfur atoms in hydrazine derivatives, thioureas and thiocarbamides and their activity as corrosion inhibitors. MNDO molecular orbital method has been employed in this study to calculate the electronic reactivity indices with full geometry optimization.

Significant correlations indicated that the variation of the corrosion inhibition efficiency with the structure of the inhibitors may be explained in terms of the computed electron properties.

Convergence of olygomer chain properties to the polymeric limits - origins of the universal asymptotic behavior

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We investigate the convergence of [X(N+1)-X(N)] and [X(N)/N] for several olygomer properties via quantum-chemical calculations for model systems. The properties considered [X] were the total energy, as well as longitudinal dipole moment, polarizability, and hyperpolarizability. The systems studied had polar and non-polar unit cells with both isolated molecules in the unit cell and connected molecular backbone. It is found that [X(N)/N] universally converges as $\{1/N\}$ due to the O(1) contribution from the chain tails to X(N). On the other hand, [X(N+1)-X(N)] asymptotically converges as $\{1/N^2\}$ in almost all cases with one exception. In particular, for the total energy of an olygomer with a non-polar unit cell, the rate of [X(N+1)-X(N)] convergence is exponential. In all the other cases the $\{1/N^2\}$ asymptotic rate of convergence can be traced to the long ranged electrostatic effects.

For longitudinal linear polarizability α, $\{1/N^2\}$ behavior can already be seen in a Clausius-Mossotti-like classical model consisting of polarizable dots. The effect of one monomer on another is $1/r^3$, where r is the distance between the monomers. Further, $[\alpha(N+1)-\alpha(N)]$ can be viewed as the polarizability of a monomer inserted in the middle of a stack of N monomers. Thus, $[\alpha(N+1)-\alpha(N)]$ differs from α_∞ by excluded effects of all monomer units from N/2 to infinity, on both sides of the chain. Integrating $1/r^3$ over the range $\sim[N/2,\infty]$ yields an $O(1/N^2)$ term. Similar arguments are valid for other properties [X] as well.

Absolute phases in Floquet theory

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We present a general Floquet theory of the dynamical role of the absolute phase in the photofragmentation of atoms and molecules subjected to laser pulses. We show how the dependance of Floquet states on an absolute phase is related to the complexity of the dressed molecular scheme and to the multiphoton character of the molecular dynamics. The theory also allows a pleasing, straightforward unification of quasi-static picture, or tunnel regime, and dressed picture, or multiphoton regime, within a single Floquet framework. The general theory is applied to the study of the photodissociation of H^{2+} in a 400 nm periodic laser pulse, repeated with a frequency lying in the IR. The dependance of the dynamics on the phase of the pulse envelope is highlighted through an effect previously called dynamical dissociation quenching (DDQ) effect and through the various kinetic energy spectra. Using wavepacket spectral techniques, we map out the Floquet content of the dynamics, i.e. its multiphoton character both with respect to the carrier-wave frequency, which gives rise to the usual bond-softening (BS) mechanism, and with respect to the pulse modulation frequency in the IR.

Applications of DFT Theory In Studies of Low Energy Electron Interactions With Biomolecules

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Interactions of Low Energy Electrons (LEE) with biomolecules such as DNA and its components have become a major interests of theoretical studies, due to the accumulation of experimental evidences that such interactions contribute to radiation damage of biomolecules. Here we report our DFT theory treatment of three aspects of such interactions:

(1) *Radiosensitization effects of halouracils* [1,2] Using the B3LYP functionals it was found that base pairing with adenine slightly decreases the EA of the halouracils, in contrast to the substantial increase in EA on base pairing of natural bases. This suggests that, the probability of electron capture by halouracils when in ds DNA are substantially reduced. Even though the activation barriers for dehalogenation are small for both BrU-A and ClU-A, only the former has negative values of both ΔH(-0.95 kcal/mol) and ΔG(-1.52), while the latter has negative ΔG(-0.28) but positive ΔH(1.27). Infinite separations into halogen anions plus the remaining AU-5-yl neutral radical are energetically unfavorable. It is found that base pairing does not change the reactive nature of the uracil-5-yl radical. The results suggest that the radiosensitization properties of halouracils should be less effective in double strand than in single stranded DNA.

(2) *DNA strand break*[3] The discovery of DNA strand breaks induced by low energy secondary electrons[4] sparks a necessity to elucidate the mechanism. Through theoretical studies based on a sugar-phosphate-sugar model that mimics a backbone section of the DNA strand, it is found that bond cleavages at 3' or 5' C-O sites after addition of an electron are possible with a ca. 10 kcal/mol activation barrier. Moreover, the potential energy surfaces show that dissociation at both sites are highly favorable thermodynamically. Though the phosphate group in DNA is not a favored site for electron attachment because of competitive electron transfer to the bases, low energy electrons which encounter a vibrationally excited phosphate may induce strand breaks even when the electron energy is near 0 eV. These findings have profound implication as low energy secondary electrons are abundantly generated by all type of ionization radiation.

(3) *Formation of hydrogen atoms from uracil.*[5] To better understand the dissociation of uracil induced by LEEs, we theoretically characterized the potential energy surfaces (PESs) along the N-H and C-H bonds of the uracil anion, as well as the energetics involved. The PESs show that, an activation barrier of less than 1 eV exists for the N_1-H dissociation, while those for C_5-H and C_6-H show a monotonic increase with bond stretching. All the N-H and C-H bond dissociations are endothermic; the adiabatic PESs suggest an energy threshold for formation of hydrogen from N-H and C-H bonds of the order: 0.78 (N_1) < 1.3 (N_3) < 2.2 (C_6) < 2.7 eV (C_5). The H-deleted uracil radicals have exceptionally high adiabatic electron affinities, i.e., 3.46 (N_1), 3.8 (N_3), 2.35 (C_5) and 2.67 eV (C_6). These high electron affinities compensate the extra energy needed to break the N-H or C-H bonds. This result may therefore explain the large hydrogen yield found experimentally from uracil upon attachment of LEEs.

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2. Xifeng Li, Michael D. Sevilla, Léon Sanche; *J. Am. Chem. Soc.* **2003**, 125, 8916.
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4. Boudaiffa, B.; Cloutier, P.; Hunting, D.; Huels, M. A.; Sanche, L.; *Science*, **2000**, 287, 1658.
5. Xifeng Li, Léon Sanche, Michael D Sevilla; *J. Phys. Chem.* B **2004,** 108, 5472-5476.

Density-Functional Studies on Peroxynitrite Oxidation of Guanine

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Peroxynitrite is a highly reactive oxidizing and nitrating agent and postulated to play an important role in oxidative damages to DNA. Guanine, which has the lowest redox potential of all nucleobases, is readily oxidized by peroxynitrite in the DNA helix and gives various direct and secondary products. Both 8-nitro-2'-deoxyguanosine and 5-guanidino-4-nitroimidazol are formed directly from the reaction of peroxynitrie and 2',3',5'-*O*-acetylguanosine. The reaction is proposed to follow pathways in which either the one-electron oxidized guanosine radical cation or the guanosine radical ($G(-H)^{\bullet}$) acts as the key intermediate.

In the present work, DFT computational methods in combination with the COSMO solvation model are applied to study the reaction mechanism of peroxynitrite oxidation of 2',3',5'-*O*-acetylguanosine. In the gas phase, the radical-radical reactions of guanosine radicals and nitrogen dioxide are studied by means of potential energy surface (PES) scans. Subsequent optimizations have located some of the transition structures. In a few of the structures, water bridges are found to be quite important in the proton transfer process.

In order to determine the relative importance of the two proposed reaction mechanisms, all local minima and maxima on the potential energy surface need be located. The solvent effect will be taken into account by using the COSMO solvation model.

A Quasiclassical Trajectory Study of Collisional Energy Transfer and Dissociation in He + H_2 (v,j) using a new Potential Energy Surface

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State-to-state rate coefficients and cross sections were calculated for He + H_2(v,j) by quasiclassical trajectories using the ab initio potential recently published by Boothroyd, Martin, and Peterson [J. Chem. Phys., **119** 3187 (2003)]. Results are compared with those of earlier calculations using the potential of Wilson, Kapral, and Burns [Chem. Phys. Lett. **24**, 488 (1974)]. Also compared are the extent of threshold elevation for collision induced dissociation and the extent of interconversion of vibrational and rotational energy. Implications for modelling the interstellar medium are discussed.

Theoretical Study of Geometries and Electronic Structures of $AlNa_n$-H (n=1-8) Clusters

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Applied chemists are interested in bimetallic cluster as a new catalyst. The adsorptive activity and reaction process on the surface of cluster are important for catalyst. In this conference, we presents the theoretical study on the geometry and adsorptive activity of $AlNa_n$ (n=1-8) clusters adsorbed a hydrogen atom, $AlNa_n$-H (n=1-8), clusters from a view point of MO theory. The possible geometrical and electronic structures of $AlNa_n$-H (n=1-8) were examined with *ab initio* molecular orbital theory. Calculation was performed by the B3LYP method with 6-311G* basis set. Stability and adsorptive activation of $AlNa_n$-H (n=1-8) were estimated with the bonding energy between Al-Na cluster and H atom. Program used was GAUSSIAN 98 and 03 program packages. The most stable structure of $AlNa_n$-H (n=1-8) is shown in Fig. 1. Hydrogen atom is adsorbed outside of Al-Na cluster except $AlNa_6$ cluster. In $AlNa_n$ (n=1-6), H atom is necessarily connected to Al and Na atoms. In $AlNa_7$ and $AlNa_8$, H atom is adsorbed on Na-Na bond, because Al atom is located in Na cage. In the case of adsorption of H atom, the distribution of LUMO or SOMO of Al-Na cluster plays an important role. For example, H atom is located in Na cage in $AlNa_6$ cluster, because SOMO is including 3p-orbital of Al distributed to Na cage. The stabilization energy by adsorption of H atom is in range of 2.0 to 2.9eV. This energy which is larger than general value of adsorption energy, becomes small with increasing Na number.

^{15}N and ^{13}C NMR Chemical Shift Calculations and the Effect of Electron-Withdrawing Groups on a Series of Pyrroles

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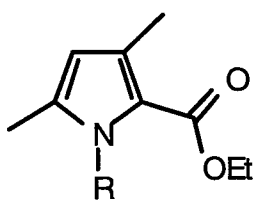
Introduction of an electron-withdrawing group (EWG) onto the nitrogen atom of a pyrrole decreases the aromaticity of the pyrrole ring and reduces the reactivity of the pyrrole towards electrophilic attack. Deshielding (shifts to lower field) of ^{13}C NMR chemical shifts was generally observed experimentally with the introduction of N-EWGs.[1] However, the experimental ^{15}N NMR chemical shifts for the N-EWG pyrroles show anomalous behavior for the acyl (Ac) and triflate (Tf) substituents (Scheme 1). Consequently, a density functional theory (DFT) study was carried out to examine the relationship between the electronic structure of pyrroles and their ^{15}N NMR chemical shifts.

A comprehensive DFT functional and basis set study was undertaken on a small number of molecules using three DFT functionals (B3LYP, B3PW91, and PBE1PBE) with several basis sets to determine the most efficient and accurate level of theory for the calculation of ^{13}C and ^{15}N NMR parameters for the pyrroles. The B3PW91 and PBE1PBE functionals were found to yield better accuracy than the widely used B3LYP functional. Furthermore, it was determined that the optimal basis set for this study is 6-311+G(2df,p). Therefore, the level of theories used for the chemical shift calculations of the pyrroles was the B3PW91 and PBE1PBE functionals with the 6-311+G(2df,p) basis set.

A correlation between the paramagnetic shift and the chemical shift was obtained for the pyrroles in Scheme 1. The dramatic changes in the nitrogen shift tensors of the pyrroles resulting from the paramagnetic term were explained using natural chemical shielding (NCS) analysis based on the contributions to the shielding from well-localized "Lewis" bonds, lone pairs, and delocalized "non-Lewis" features in the electronic structure. Based on the NCS analysis, changes in the σ(N5-R)-π^* transitions my account for the nitrogen chemical shift trend observed in this series of pyrroles. Moreover, the change in the sum of the σ(C1-N5)-π^* and the σ(C4-N5)-π^* transitions may account for the chemical shift trend observed. Thus, for the pyrroles studied, a simple correlation between the nitrogen chemical shifts and the EWG strength cannot be general since many factors contribute to the total value of the chemical shift.



$R^1 = H$ $R^5 = COO^tBu$ (-Boc)
$R^2 = CH_3$ (-Me) $R^6 = SO_2CH_3$ (-Ms)
$R^3 = CH_2Ph$ (-Bn) $R^7 = SO_2CF_3$ (-Tf)
$R^4 = COCH_3$ (-Ac)

Scheme 1

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Recollision Effects in Ionization -- H_2 case

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Exact 2-D calculations of single and double ionization for H_2 have been performed at 780 nm and high intensities in order to investigate the effect of recollision on the ionization dynamics of H2. Comparision is also made with Time-Dependent Hartree-Fock and Density Functional approaches.

Coarse-grain molecular dynamics study of interactions between transmembrane nanotubes

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A generic nanotube functionalized with hydrophilic termini can insert into a biomembrane, forming a nanopore. The direct and membrane-mediated interactions between these nanopores can lead to their aggregation and has implications for the design of synthetic channels and antibiotics. The role of hydrophobic/hydrophilic matching is examined in this context. Specifically, the loss of stability due to the hydrophobic/hydrophilic mismatch is quantified by measuring the free energy of the meniscus. Then, an attempt is made to relate this free energy to the aggregation propensity.

Diffusion in channeled structures

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The theory of Ronis and Vertenstein [J. Chem. Phys. vol. 85, 1628, (1986)] is used to calculate the permeability of noble gases in channeled structures. The diffusion of Xenon in Theta-1 and of argon in quartz were both studied. The first of these systems is made of one-dimensional, disconnected channels. The second contains interconnected three-dimensional channels. The free energy barriers in Theta-1 are considerably lower than the ones in quartz. The required time-correlation functions are obtained from numerical simulations performed using a small number of target crystal atoms. The dynamics of the target atoms reproduce those of the full crystal by the means of a Langevin equation of motion. An approximate expression for the potential of mean force inside the crystal is derived. The permeability is reported and compared in detail with that obtained from transition state theory.

Simulation of thermodynamic properties of graphite-based hydrogen storage materials

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Molecular hydrogen (H_2) offers a promise of the ideal material for production of electricity in transportable devices, such as fuel cells. However, sufficiently dense hydrogen storage at near-ambient conditions remains a challenge. The main attractive interaction of non-polar H_2 molecules is long-range London dispersion, which is enhanced by strongly polarizable physisorption substrates such as nanostructured graphite platelets (graphene). Graphene is also light-weight, cheap, chemically inert and environmentally benign. While the binding enthalpy in the H_2-graphene system is well-established, the free energy remains a controversial subject.

A major difficulty in theoretical simulations of H_2 binding free energies arises due to quantization of nuclear motion, which becomes significant at temperatures not far below ambient. Here, we solve rotationally averaged, three-dimensional Schroedinger equation for the motion of H_2 adsorbed on graphite surfaces. The eigenspectrum of the nuclear Hamiltonian is then used to evaluate quantum-mechanical partition functions, and binding free energies.

The results of our calculations demostrate that graphene surface is not a viable H_2 storage material, with binding free eneries of ca. -1 kJ/mol (T=300K). At the same time, multilayer graphene nanostructures show binding free energies of ca. -5 kJ/mol, tunable by the interlayer separation. Such free energies may already prove useful for storage-enhancing materials.

Three-dimensional simulation of photoelectron rescattering in strong laser fields

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We solve the time-dependent Schrödinger equation in three dimensions for $H_2^{(1+)}$ in a one-cycle laser pulse of moderate intensity. We consider fixed nuclear positions and Coulomb electron-nuclear interaction potentials. We analyze the field-induced electron interference and diffraction patterns. To extract the ionization dynamics we subtract the multiphoton excitations to all signicant low-lying bound states explicitly. In the simulation we follow the time evolution of well-defined wavepacket, that is formed near the first peak of the laser field. We observe the subsequent fragmentation of the wavepacket due to molecular focusing. We show how to retrieve the diffraction image by taking the ratio of the momentum distributions in the two perpendicular directions. Even at moderate laser intensities, the position of the diffraction peaks is well described by the classical slit diffraction rule.

Basis Set Effects on the Geometrical Parameters of Small Selenium Compounds

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Theoretical investigation of biologically relevant selenium compounds has not been studied extensively. The first step in the study of these important biological catalysts is the establishment of a good computational method for the treatment of these compounds. To identify the optimal computational method for the treatment of organoselenium compounds we have investigated the performance of various levels of theory and basis sets for a selected set of ten organoselenium structures that serve as models of larger selenoenzymes and other selenium-containing catalytic intermediates.

Molecular Dynamics of Iron Cations in Water

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Theoretical investigations about the interaction of Fe^{2+} and Fe^{3+} with water date back to more than 25 years and many have appeared in the literature since then. There are different reasons for this interest: The strongly nonadditive effects in the interaction of the cations with water; the acidity of its solutions and the reactions related to it; the two different oxidation states that iron ions can assume; the fact that iron, as a transition metal, interacts with its environment in a more complicated way compared to, for example, alkali ions. We review former theoretical investigations and present two new simulation experiments: In the first one we use a newly developed flexible water model (SPC+CCL) in molecular dynamics simulations of solvated Fe^{2+} and Fe^{3+} ions together with an effective ion-water potential. We show that this potential manages to reproduce structural and dynamical properties of the solution. In the second one we use the Car-Parrinello method to study the solvation of a single Fe^{3+} ion, without the use of explicit potential functions, in a box containing 32 water molecules.

Diffusion and Viscosity of Colloidal Hard-Sphere Suspensions: A Statistical Mechanical Approach

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A theory of the diffusivity of colloidal hard-sphere suspensions is formulated by exploiting the generalized excluded volume effect described by the generic van der Waals equation of state for colloidal hard spheres in solvent. The theory predicts a crossover behavior in the effect excerted by solvent molecules on colloidal hard spheres immersed therein. Namely, above a critical colloidal volume fraction (φ_c=0.38), solvent gives rise to a lubrication effect on the diffusion of the colloidal particles, bringing about an enhanced diffusivity, whereas, below φ_c, they play as a barrier against the colloidal particle diffusion, reducing the diffusivity. The agreement between the theory and experiment is found to be excellent over the entire volume fraction range investigated by experiment thus far: up to about 0.60 in the colloidal volume fraction. Also presented is a statisical mechanical expression for the viscosity of the collidal suspensions that accounts for the experimental results in an excellent accuracy.

Vibrational Energy Levels of Ammonia With Wave Number Accuracy From First Principles Calculations

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The vibrational spectrum of ammonia is calculated variationally using potential energy surface obtained with the latest methods of electronic structure calculation. The centrally bound ammonia-type molecules are interesting systems to study, due to the combination of the large-amplitude inversion motion and five high-frequency modes. This facilitates the study of capabilities and feasibility of the latest theories in molecular physics and quantum chemistry and their numerical application.

The vibrational kinetic energy operator, which is exact within the Born-Oppenheimer approximation, is applied, and the six-dimensional vibrational variational problem is solved effectively using successive basis set contractions and full symmetry of the systems. The six-dimensional potential energy surface is expressed as Taylor-type series expansion. The electronic energies in the complete basis set limit are obtained using the explicitly correlated CCSD(T)-R12 method for the most essential parts of the surface, and basis set extrapolation for the rest of the six-dimensional surface. These energies are stepwise scaled to the full configuration interaction limit, employing higher than SD(T) excitations up to pentuples in the coupled-cluster series. All electrons are correlated and the one-electron scalar scalar relativistic as well as the diagonal Born-Oppenheimer corrections are added. Results with 1 cm^{-1} accuracy are obtained for inversion levels, inversion splittings, and lowest high-frequency states.

Hydration-parameterized continuum electrostatic models

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Solvent environment has profound effects on the structural, thermodynamic and kinetic properties of biomolecules. The essential dielectric and nonelectrostatic characteristics of the solvent can be represented by a continuum approximation, which is a computationally efficient alternative to explicit molecular representations of the solvent. Using molecular mechanics force field partial atomic charges and a boundary element continuum dielectric method for calculating the electrostatic component of the solvation free energy of a molecule, we investigate the transferability of parameters for the electrostatic component of solvation calibrated using small molecule hydration transfer free energies to binding free energy calculations. We show the non-uniqueness of parameterization of continuum electrostatic models with respect to the solute atomic radii and interior dielectric constant based on hydration (vacuum-to-water transfer) free energy data available for 210 small molecules. Parameter sets that are optimal and equivalent for hydration free energy calculations yield large variations in the calculated absolute and relative electrostatic binding free energies between trypsin and various benzamidine-class inhibitors. Thus, parameterization of solvation effects based on hydration data is not sufficient to guarantee its transferability to the calculation of binding free energies in solution.

Insights into the crystal/liquid interface of Lennard-Jones spheres and water

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The interface between a solid and liquid is difficult to probe experimentally, in order to achieve an understanding of the microscopic processes involved in such an interface, molecular dynamics simulations were performed on Lennard-Jones spheres (LJS) and water. Through the use of a new simulation technique growing crystals of ice and LJS were obtained under non-equilibrium steady-state conditions. In this paper, we will report growth rates of different crystallographic faces of ice and LJS. In addition we will show new results that describe the position, interfacial width and microscopic structure of the interface of growing crystals.

Density functional theory applied to molecular quantum dots

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In recent experiments, molecular quantum dots (MQDs) that exhibit the Kondo effect have been investigated. Here, we model a MQD by means of density functional theory. The system studied is a cobaltocene molecule attached to two semi-infinite gold contacts. We use the Kohn-Sham approach to determine the electronic structure of a finite-cluster model for the MQD. Furthermore, employing the Kohn-Sham method combined with Landauer's formula, we calculate the conductance of the system. The results of our simulations depend on the approximate exchange-correlation functional employed. The zero-voltage conductance obtained with PBE hybrid is much smaller than that calculated with PBE or LSD. The implications of using density functional theory for the calculation of the molecular conductance are discussed.

Resonant Transfer of Excitation Between Two Molecules: A General Formula Obtained From Quantum Electrodynamics

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The theory of molecular quantum electrodynamics is used to calculate a general formula for the matrix element for the resonant exchange of energy between two molecules. This simplest of intermolecular interactions is mediated by the transfer of a single virtual photon between an initially excited donor species, and an acceptor body in the ground state. Each moiety is described as having an electric multipole moment of arbitrary order. Standard time-dependent perturbation theory together with diagrammatic techniques is employed to evaluate the matrix element, with the Fermi golden rule subsequently being used to obtain the generalized rate of energy migration. The expression derived is applicable to all donor-acceptor separation distances beyond the region of overlap of molecular electronic wavefunctions.

Application of the theory developed includes computation of excitation transfer rates between dipole-quadrupole, quadrupole-quadrupole, and dipole-octupole systems, as well as to the widely known dipole-dipole example. A new and interesting feature arises from the use of irreducible components of the octupole moment tensor. For instance, the weight-1 term contributes only to the retarded transfer rate, and appears as a higher-order correction term to the exchange of excitation between two dipole entities. The asymptotic behaviour of the rate is also examined in the limit of large and small separation distance for each of the interactions considered in order to provide insight into the underlying mechanisms associated with resonant transfer of energy.

Effect of Laser Phase on Reaction Paths in Laser-Induced Chemical Reactions

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Potential surfaces, dipole moments and polarizabilities are calculated by ab-initio(MP2) methods along the reaction paths of the F + CH_4 and Cl + CH_4 reaction systems. It is found that in general dipole moments and polarizabilities exhibit minima and maxima respectively near the transition state. Interaction with infra red (IR) intense laser fields leads to the possibility of interferences between the dipole and polarizability laser-molecule interactions. The larger dipole moment in the Cl + CH_4 reaction can lead to the creation of deep wells (instead of energy barriers) and new strongly bound states in the transition state region. This suggests reshaping of potential energy surfaces and possible coherent control of reactivity along reaction path as a function of the absolute phase of the incident field.

Calculating the A term of Magnetic Circular Dichroism with Time Dependent Density Functional Theory

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In the presence of a magnetic field, all substances will rotate plane-polarized light similarly to the well-known property of chiral substances. Also similarly to chiral substances, if a sample is immersed in a magnetic field, it will absorb left and right polarized light with differing absorption coefficients, an effect known as magnetic circular dichroism (MCD).

An MCD spectrum can be derived by plotting the absorbance difference as a function of photon energy. Such spectra have proven useful for deducing molecular structure, the symmetry and magnetic dipole moment of excited states and for assigning absorption spectra. Each signal in an MCD spectrum is made up of three contributions, commonly called the $\mathscr{A}$, $\mathscr{B}$ and $\mathscr{C}$ terms.

A method to calculate MCD $\mathscr{A}$ terms within the formalism of time-dependent density function theory (TD-DFT) of molecules with non-degenerate ground states will be described. The implementation is relatively straightforward simply requiring the magnetic and electric dipole moment integrals over the molecular orbitals of the ground state and the $\boldsymbol{F}$-vector derived from the solution of the TD-DFT equations. Some example calculations will be described including such molecules/ions as MnO_4^-, $Ni(CN)_4^{2-}$ and hexachlorobenzene.

Molecular energy derivatives for state-universal and valence-universal multi-reference coupled-cluster methods: theory and pilot application to HF dipole moment curves

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The theory for computation of molecular energy derivatives using state-universal and valence-universal multi-reference coupled-cluster methods is presented. A state-dependent constrained variation approach is made use of in these developments. Its relation to generalized algebraic elimination based Z-vector technique of Handy and Schaefer is discussed in multi-reference context. A pilot application to generate dipole moment curves of ground and three low-lying excited states of HF molecule using state-universal multi-reference coupled-cluster method is presented and discussed.

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Relativistic DFT Study of the UO_2^{2+} and UO_2^{+} Complexation With Expanded Porphyrins

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Nuclear waste typically contains both actinides (mostly U, Np, Pu, Am) and their fission products (lanthanides, Cs, Tc). Treatment of nuclear waste involves either separation of the actinides as useful commodities (for reuse as nuclear fuel, for example) or their immobilization for further storage.

One of the methods proposed involves the coordination of actinide ions with polydentate macrocyclic ligands. During the last decade, Sessler and co-workers [1] have developed a new class of N-donor pyrrol based macrocycles, called expanded porphyrins, capable of forming stable complexes with actinyl ions.

Theoretical studies of these complexes could help to develop new, more efficient ligands tailored for selective coordination with specific elements and/or oxidation numbers. However, modeling of actinide complexes is a difficult task because of the importance of electronic correlation and relativistic effects. Moreover, the computational method should be effective enough to handle systems of such size. Recently, it has become possible with the development of modern DFT techniques and robust relativistic approximations. An example of such a modern technique is a method proposed by D.N.Laikov [2,3] that employs fast XC fit and scalar four-component all-electron DFT, implemented in the program Priroda.

We have evaluated that method by comparing its results with experimental thermodynamic and structural data available for small molecules and with the theoretical results given by other methods [4].

We have done calculations for the UO_2^{2+} and UO_2^{+} complexes with some of the expanded porphyrins proposed by Sessler [1] and compared the results with the available experimental data. Specifically, we have investigated unsubstituted analogues of the alaskaphyrins, dioxamethyrin, isoamethyrin, oxasapphyrin, sapphyrin, pentaphyrin and texaphyrin. Complexation energies against free ligand dianion were calculated, and the nature of the uranyl – ligand bonds was examined.

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High-order adiabatic representations of quantum systems through a perturbative construction of dynamical invariants

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A perturbation theory type series is derived for the systematic construction of a dynamical invariant (or Lewis invariant) for a time-depended Hamiltonian which is characterized by a time-scale parameter t, as appears in the usual formulation of the adiabatic theorem. The derivations make efficient use of the quantum averaging method, and the obtained perturbative series permits the construction of the invariant in successive orders in $e = 1/t$, corresponding to high-order adiabatic approximations. Taken to all orders, the series yields an exact invariant for systems such as a harmonic oscillator linearly driven by an external field, while for a laser-driven two-level system, we have been able at the moment to construct an invariant up to fifth-order in the adiabatic parameter. The construct is applicable also to Floquet hamiltonians and, in this context, it furnishes high-order to exact adiabatic representations for the time-evolution of Floquet states associated with a material system in an aperiodic laser pulse. An exact Floquet dynamical invariant, defining exact adiabatic transports of Floquet states, was obtained for a laser-driven harmonic vibrational mode.

Calculation of ^{19}F NMR Chemical Shifts in Uranium Complexes Using Density Functional Theory and Pseudopotentials

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The ^{19}F NMR nuclear shieldings of fluoride ligands in uranium complexes UF_nCl_{6-n} (n=1-6) have been studied quantum chemically, using different exchange-correlation functionals and a relativistic small-core pseudopotential on uranium. In contrast to a recent study (*G. Schreckenbach, S. W. Wolff, T. Ziegler, J. Phys. Chem. A 2000, 104, 8244*) we find that pseudopotential methods are well suited for calculations of ligand chemical shifts in actinide compounds, provided that a sufficiently small core-size definition is used. With modern relativistic small-core pseudopotentials and gradient-corrected density functionals we obtain results of the same accuracy as were found with all-electron density functional ZORA or Pauli calculations. The unusually large dependence of the shifts on the exchange-correlation functional is discussed in the context of the description of σ- and π-bonding, and also with respect to the accuracy of the optimized structures.

Density Functional Study of Small Beryllium Clusters

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Beryllium clusters exhibit dramatic changes as a function of size. The bonding evolves from van der Waals-like (in Be_2) to metallic sp hybridized electronic bands (Be_n, n>7). The changing nature of sp hybridized molecular orbitals (Mos) with cluster size must affect the relative stability of different geometric cluster isomers. To study this, we did Kohn-Sham theory calculations on clusters with two to twenty Be atoms. We used the local spin density approximation for exchange-correlation and a 6-311G** basis set. We searched for the global energy minimum with an algorithm called "Tabu Search in Descriptor Space" (TSDS). We find in the small size range (n=2 to 5), the energetically favored structures are like high symmetric rare-gas clusters. At n=6 and 7, the structures are distorted octahedron and distorted pentagonal bipyramid. And for n >=8, Be_n clusters generally adopt structures that resemble oblate fragments of the hcp crystal. We will report the energetically favored Be_n cluster structures and size evolution of the cohesive energy and Mulliken populations

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Poster Session B, Tuesday afternoon

Collision-induced Alignment of Drifting Molecular Ions

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Results will be presented from recent molecular dynamics simulations of molecular ions drifting in an atomic bath gas under constant external electric field. In particular, alignment of the rotational angular momentum will be investigated. When the electric field is not weak, collisions between the ion and bath gas induce an alignment of the average rotational angular momentum in a direction perpendicular to the field.

In our previous studies, we have developed a series of approximate distribution functions that can accurately approximate the distributions obtained from the simulations. In particular, we have introduced forms for approximating the velocity-averaged rotational distribution function, as well as the more detailed velocity-rotational distribution function.

While the ensemble-averaged rotational alignment is negative (perpendicular to the field), our calculations have shown that as a function of velocity and angular momentum, the alignment takes on a much richer structure, and in fact, part of the ensemble of ions (in particular, ions with low relative velocities) actually have a positive rotational alignment, that is are aligned with their angular momentum vectors parallel with the field rather than perpendicular to it.

Results to be presented include rotational alignments of non-linear ions, with detailed calculations of $H2O^+$ drifting in helium serving as an example. As well, preliminary analysis of cross-correlation functions of velocity and angular momentum will be given. These functions correlate components of the velocity and/or angular momentum perpendicular and parallel with the field with themselves and each other. These correlation functions give a timescale for energy flow between different modes of the system, and also show which modes are most strongly coupled by collisions.

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A Preconditioned Fourth-order Runge-Kutta ODE integrator for Solving the Time-Dependant Schrodinger Equation.

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If one uses an iterative method to solve the time-independent Schroedinger equation it is straightforward to use a preconditioner to drastically reduce the number of matrix-vector products required. Preconditioned methods for solving the time-dependent Schroedinger equation are not as well developed. Common techniques such as the Chebyshev, short iterative Lanczos, split operator and simplectic methods are all used without preconditioning. Here we test a fourth-order preconditioned Runge-Kutta scheme. The key idea is to solve the Schroedinger equation in the interaction representation. This was suggested by Zhang and by Tannor. The Hamiltonian in the interaction representation is explicitly time dependent but the Runge-Kutta method allows one to propagate without approximating exponential operators in small time intervals. The use of a good preconditioner allows one to take large time steps without losing accuracy. A modification proposed by Saad reduces the number of applications of the preconditioner per time step by a factor of two. An explicitly time-dependant problem arising from quantum control theory is chosen in order to demonstrate the efficiency of the new method. For this problem, the split-operator method needed roughly 10 times more matrix-vector products than the scheme proposed here.

Calibration of a DFT-based Computational Scheme for the Study of Halide-Solvent Complexes

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In this paper, we propose a DFT-based computational scheme for the study of halide-solvent monosolvate complexes. The geometric and energetic parameters are calibrated against those obtained using the G2 and CCSD(T) methods. The two methods agree to within 2 kcal mol^{-1} for ammonia and water complexes and hence provide a good internal benchmark for accuracy in binding energies. The discrepancy in the formaldehyde system is a cause for further investigation. It is conclusively verified that the study of anions is unreliable when performed without diffuse functions on heavy atoms. Additionally, the use of diffuse functions on hydrogen atoms is also required. The basis set convergence level for geometry is obtained at the B3LYP/6-311++G(3df,2pd) level. The binding energies obtained at this level agree closely with the G2 results and also contain negligible BSSE.

Application of Core Trace algorithm for determination of Protein Backbone

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X-ray crystallography is the most powerful tool available to provide detailed three-dimensional structural information of proteins and other macromolecules. The final process of interpreting an electron density map is typically performed by a human crystallographer at a computer graphics terminal with the help of molecular visualization software. It may take weeks to months of the researcher's time examining complex three-dimensional patterns of electron density. The process is further complicated by a number of sources of noise that can perturb the density and obscure the underlying structure. Therefore, model-building is one of the primary bottlenecks impeding the progress of structural biology.

The critical point analysis is one of the common approaches which are used to determine a protein backbone. The basic approach of the method is to generate a critical point map to represent an electron density map. Generally, the critical point graph is constructed where vertices represent peaks, i.e. point of maximum density, and edges represent passes, i.e. maximum point in the path connecting two peaks. In the medium resolution of the electron density map (~3Å), peaks can be associated with the residues in the protein backbone and passes can be associated with the bonds between residues. So, the critical point graph captures the important feature of the protein, e.g. the protein backbone can be represented by one or more path in the graph. The determination of a critical point is normally from an electron density function which specifies the electron density at any point in the map. In fact, evaluation of the function is very difficult because many parameters are needed.

In this paper, the core trace algorithm is proposed to determine the critical point in the electron density map without using density function. It is easily understood and implemented. The core trace algorithm assigns a special feature number to the local maximum (peak) and tries to merge the neighboring lower density points to the nearby peak and forms a distinct, local and growing nodule. As the map is examined, eventually these nodules will touch together. In the end, the electron density map is partitioned into many small, compact volumes. In each volume, the point with the highest density is the peak. Each volume touches other volumes and the highest point in the boundary is the pass between them. The critical point graph is created by connecting the peaks together with the help of the pass information.

Testing on both ideal and experiment data at medium resolution for proteins shows that the core trace algorithm is effective for interpretation of the electron density map. Normally, ~90% of the residues in the protein backbone are covered by the critical point map. Furthermore. It is observed that each residue in the polypeptide chain is generally covered by one peak. However, the segment correctness is still low. We attempted to delete as many wrong segments as possible without deleting the correct segments in the critical point graph. In the end, the segments can be accounted for ~80% residues in the protein backbone with ~80% correctness (Table 1). Though the system is based on proteins with known structure, it is expected that the system can be applied to determine the protein backbone for unknown structure.

Table 1 The properties of the final segments

Protein code	Segment #	Coverage (%)	Correctness (%)
1a0b	1	90.60	97.25
3apr	13	77.88	84.26
1cgt	30	80.70	81.90
1pax	13	86.86	80.21
1tfr	12	77.74	80.59
2cyp	11	86.35	88.46
1msi	4	84.85	82.35
2fcr	7	72.83	82.35
2ptd	14	71.28	82.75

A Theoretical study of Nitrogen-Rich Phosphorus Nitride $P(N_n)_m$

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Ab initio calculations predict that structures $P(N_n)_m$ (n=3, 4; m=1-4, tetrahedral nitrogen and square N_4, and linear N_3) to be local energy minima characterized by all real vibrational frequencies. Phosphorus atom looks like an anchor to grasp nitrogen clusters and it prefers odd bonds although some stable structures with even bonds optimized to be minima. The special role of phosphorus atom in the geometrical arrangements of these systems was also investigated. The low barriers of $P(N_4)_m$ in gas phase mean that these nitrogen-rich phosphorus nitride require external stabilization if they are to be used as high-energy density materials or other starting materials.

The results confirm our initial suggestion that a phosphorus atom can indeed "concentrate" several nitrogen clusters around itself, due to the presence of valence shell *d*-orbitals. The gas phase molecules $P(N_4)_m$ correspond to stable energy minima, that is, they are stable on thermodynamics grounds, but the kinetic stability of molecule $P(N_4)_3$ is critical because of a low barrier height. A condensed phase reaction could eventually be the optimal choice. In such a case, the actual charges at various nitrogen atoms in the context of interactions between neighbor molecules will likely become important factors that may also complicate the problem of energy storage considerably. It is suggested that these molecules could provide a new approach for storing metastable nitrogen clusters or as starting materials.

Refining contracted basis Lanczos methods for computing rovibrational levels of methane-like molecules.

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We shall discuss several extensions of our contracted basis Lanczos method for computing rovibrational levels of methane. A new C_{3v} invariant quadrature grid is used to calculate levels labelled by C_{3v} irreducible representations. This grid is also useful for CXY_3-type molecules. This is demonstrated by calculating levels of CH_3D. High J methane rovibrational levels as well as results on a global potential surface of Marquardt and Quack will also be presented. We shall also discuss further optimization of the basis set.

Properties of Modified DNA Components: Searching for a Universal Nucleobase

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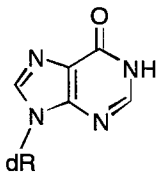
Modified DNA components are used in a wide variety of biochemical applications including polymerase chain reaction (PCR), hybridization probes and antigene or antisense therapeutics. These applications are based on selective binding of a modified oligonucleotide to a specific base sequence within DNA (or RNA). This selective binding is possible due to the complementary base pairing rules of natural nucleobases.

One potential problem with these techniques occurs when one of the bases in the target DNA strand sequence is unknown. In these instances, a degenerate base, which binds with either the purines or pyrimidines, or a universal nucleobase, which binds equally with all four natural bases, would be extremely useful. We report computational studies of the properties of various modified DNA components that have been studied as potential universal or degenerate bases. The structures of some of these molecules are shown below. The goal of our work is to aid the design of more efficient modified nucleobases in the future by first better understanding the properties of molecules that are currently used for these applications.



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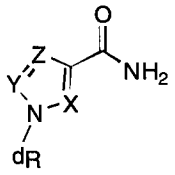
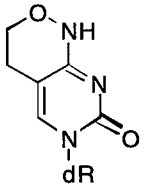


Azole Carboxamides



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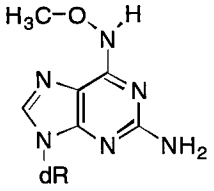

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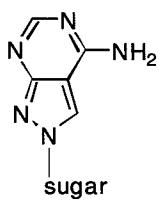

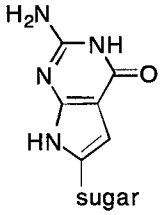

Modified Purines

Vibrational Relaxation and Photodesorption of NO/Pt(111) : A Density Matrix, Multi-Dimensional and Multi-Phonon Study

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The effect of vibrational relaxation on the photodesorption dynamics of NO from a Pt(111) surface has been investigated theoretically. Although this system has been studied in many previous works, the relaxation of NO stretching vibration due to the interaction with electron-hole pairs in metals has not been included in conventional models. Although the relaxation lifetimes of the first-excited vibrational state of diatomic molecules adsorbed on metal surfaces are generally in the range 0.1–1 ps, the desorption dynamics of NO complete in about 1 ps. Therefore, it is considered that the vibrational relaxation can influence the vibrational state of this stretching mode during the desorption process.

We described the desorption dynamics by using the time propagation of the density matrix. The effects of vibrational relaxation were included by using a Redfield-like model. We also investigated the validity of the parameters for dynamical calculations by *ab initio* methods. As a result, we obtained physically reasonable results for the desorption probability, the mean translational energy, and the vibrational state distribution for the desorbed NO molecules [1].

Another degrees of freedom and surface motions are also included and their influence is evaluated using the Golden rule formula [2].

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Empirical Energy Function for neutral or charged metal clusters formed by pure or mixed elements

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An empirical energy function for neutral or charged metal clusters formed by pure or mixed elements was developed by combining the Scaled Morse Potential (SMP) and the Modified Charge Equilibration method. The SMP is an empirical function that allows very easy and reasonably accurate calculation of energies for neutral and homonuclear metal clusters of elements in group IA, IB, and a few others. But the SMP is unreliable when ionic effects become important because it is based on a purely covalent picture of bonding. To correct this deficiency we implemented the Charge Equilibration (Qeq) method. The Qeq method developed by Rappe and Goddard [J. Phys. Chem. 1991, 95, 3358] gives us an easy way to predict the charge distribution within a system. But unfortunately it often overestimates the charge transfer. For instance, the Qeq unphysically gives an artificial charge transfer amount 0.4e for a gas-phase sodium chloride molecule with large separation. Instead of introducing some constraints to avoid unphysical charges, we cut off the Taylor Expansion of Energy w.r.t charge at the 4^{th}-order term inclusively while the highest order included in usual Qeq is 2. This modification requires an iterative calculation because of the nonlinear relationship between energy and charge. We applied our method to clusters consisting of Ag and Li atoms and the results so far agree rather well with DFT calculations. Further applications are on the way.

Transport properties of atomic and molecular nanowires

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We present a simple method to calculate the transport properties of nanowires and molecules that is based on Landauer's formula.Within a self-consistent tight-binding method, the zero-bias conductance of short gold wires is obtained. We find considerable conductance variations with one conductance quantum being the upper limit. Combining Kohn-Sham DFT with tight-binding we calculate the *I-V* curves of several molecular wires, such as octanedithiol (C8), benzenedithiol (BDT), terthienyldithiol (T3), oligo(phenylene-ethynylene)dithiol (OPE) with and without amino-(OPE-NO_2) and nitro- amino- (NH_2-OPE-NO_2) functionality. We treat the supermolecule (finite gold clusters plus molecule) with DFT and the infinite gold contacts with tight-binding. The dependence of *I-V* curves on different potential profiles is discussed. Our method is then applied to a photochromic switch molecule (dithienylcyclopentenes (DTCP)). The calculated switch ratio of the closed and open form agrees qualitatively with experiment.

Ab Initio Molecular Dynamics Studies of Bimolecular Reactions

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Studies of the free energy of reaction of bimolecular reactions calculated by thermodynamic integration in combination with ab initio molecular dynamics are described. The reactions studied include the Diels-Alder reaction, the acid-base reaction of H_2O and BH_3, cycloproponation of ethene with dichlorocarbene and the ketene dimerization. Reasonable agreement with more convention frequency analysis calculations is obtained if a) the slow growth thermodynamic integration is slow enough or pointwise integration is used b) the Andersen stochastic thermostat is applied c) appropriate corrections are added to allow for the degrees of freedom removed by constraining rotation and translation. The Nosé thermostat is found to perform poorly for these reactions.

Optimizing the Structures of Reactants, Products and Transition States on the Free Energy Surface

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Traditionally the structure of reactants, products and transition states (TS) of chemical reactions, as well as the free energy changes, have been calculated by static quantum chemical approaches, within the harmonic approximation. However, this procedure might not be adequate for TS's in chemical reactions where weak intermolecular forces dominate. Presented here is an algorithm for performing the optimization of structures for reactants, products and TS on the free energy surface (FES) based on the ab initio molecular dynamic (AIMD) simulations. Several simple elementary reactions, which belong to Lewis acid/base addition and S_N2 reactions respectively, were studied: (1) $BH_3 + H_2O \rightarrow H_2O{\bullet}BH_3$, (2) $BF_3 + NH_3 \rightarrow BF_3{\bullet}NH_3$, (3) $NH_3 + BH_3{\bullet}NH_3 \rightarrow NH_3{\bullet}BH_3 + NH_3$, (4) $HO^- + CH_3I \rightarrow CH_3OH + I^-$. The results show that the structures of reactants, products and TS on FES differ from the ones on PES. For the Lewis acid/base reactions 1 and 2, there are no TS on the PES, but the TS structures have been located on the FES and the TS structures shift to be more the product-like with increasing temperatures. For the S_N2 reactions, the B-N and C-O/C-I distances in the TS will elongate with increasing temperature.

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