

DIVISION OF PHYSICAL CHEMISTRY

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Making and Breaking Chemical Bonds in Gas and Condensed Phases

Abstracts

PHYS 6 [635245]: Reactivity patterns of cytochrome P450 in oxygen transfer reactions: The protein, the active species and the chameleon

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The active species of the cytochrome P450 enzyme is a high-valent iron-oxo species, so-called Compound I (Cpd I). I shall show that Cpd I behaves like a chameleon species that adopts its geometry and electronic structure to the protein environment in which it is accommodated, and that it changes its reactivity and selectivity patterns under the influence of hydrogen bonding and polarization effects, which mimic the protein environment [Schöneboom, et al. J. Am. Chem. Soc., 124, 8142-8151 (2002); De Visser, et al. Angew. Chem. Int. Ed., 41, 1947-1951 (2002)]. Using a chameleon species in many different protein environments is one of the ways by which the enzyme modulates its selectivity. The Chameleon oxidant can serve as a new paradigm in enzyme catalysis.

PHYS 7 [637303]: Modeling chemical reactions in proteins by the QM/MM method based on the flexible effective fragment potential technique

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Development and applications of a new approach to hybrid quantum mechanical - molecular mechanical (QM/MM) method, which is based on the effective fragment potential (EFP) technique (M.Gordon et al., J.Phys.Chem.A, 2001, 105, 293), are presented. Compared to the original formulation of the EFP theory, we introduce flexible chains of small EFs and replace EFP-EFP interactions by the MM force fields. The concept of effective fragments is also utilized to solve the QM/MM boundary problem across covalent bonds. The main emphasis of this approach is on modeling chemical reactions in protein environments. Parameters of effective fragments corresponding to the principal units of aminoacids can be obtained in preliminary ab initio calculations. The applications include modeling chemical transformations for the serine protease enzymatic reaction, proton transfer over chains of water molecules in ion channels, hydrolysis of guanosine triphosphate by the Ras-GAP protein complex.

PHYS 8 [643307]: Simulation of chemical reactions in enzymes with a density functional theory QM/MM free energy method

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The density functional theory QM/MM free energy method for simulation of chemical reactions in enzymes will be presented. The method features (1) a pseudo-bond QM/MM approach to a smooth interface between the QM and MM regions, (2) an efficient iterative optimization method to determine optimized structures, (3) an efficient search of minimum energy paths for a system with thousands of atoms on the QM/MM potential and (4) a free energy perturbation approach to calculate the potential of mean force along the reaction path. Recent applications and comparison with experimental studies will be presented.

PHYS 9 [639538]: Heterolytic OH bond breaking in the condensed phase: prediction of carboxyl pKa's in proteins using QM

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A computational methodology for protein pKa predictions, based on ab initio quantum mechanical treatment of part of the protein and linear Poisson-Boltzmann equation treatment of the bulk solvent, is presented. The method is used to predict and interpret the pKa's of the five carboxyl residues (Asp7, Glu10, Glu19, Asp27, and Glu43) in the serine protease inhibitor turkey ovomucoid third domain. All the predicted pKa values are within 0.5 pH units of experiment, with a root mean square deviation of 0.31 pH units. We show that the pKa lowering observed for some of the residues is primarily due to hydrogen bonds (HBs) to the carboxyl oxygens. HBs involving amide protons are shown to be particularly important, and the effect of H-bonding is shown to be non-additive. Hydrophobic effects are also shown to be important in raising the pKa. Interactions with charged residues are shown to have relatively little effect on the carboxyl pKa's in this protein, in general agreement with experiment.

PHYS 10 [643146]: The floating occupation molecular orbital reparameterized semiempirical configuration interaction method: Direct photodynamics for large chromophores in proteins and condensed phases

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First principles simulations of photodynamics have recently been demonstrated using the ab initio multiple spawning (AIMS) method. The AIMS method uses a multireference wavefunction ansatz in order to achieve a globally accurate description of the ground and excited state potential energy surfaces and their nonadiabatic couplings. AIMS has been applied to molecules with up to 26 atoms; however, the extreme computational expense poses a serious obstacle to studies of large molecules and complex environments. We describe a floating occupation molecular orbital (FOMO) semiempirical configuration interaction (CI) method which ameliorates these difficulties and demonstrate its utility for photoactive protein dynamics. Electronic orbitals in the FOMO approach are determined by optimizing an ensemble energy using fractional (floating) occupation numbers within the framework of conventional SCF procedures. These orbitals are used in a subsequent CI expansion which describes the pure states. A complete active space (CAS-CI) expansion is generally chosen, although this is not essential. The floating occupation technique ensures the correct orbital degeneracy when needed, for example in case of dissociation processes or metal-containing molecules. Virtual orbitals are partially occupied and variationally optimized, enhancing convergence of the subsequent CI expansion. The FOMO method may be applied in the context of semiempirical or ab initio wavefunctions. Because semiempirical methods were not extensively parameterized for excited states, reoptimization of the semiempirical parameters based on high quality ab initio or experimental data is often necessary when they are chosen. The FOMO-CASCI method has been incorporated in MOPAC, including the possibility of a hybrid quantum mechanical/molecular mechanical (QM/MM) description. Using the QM/MM decomposition, we treat the chromophore and possibly a small part of the environment using the FOMO-CASCI method. The remainder of the system is modeled with a classical force field method. Furthermore, we have incorporated the FOMO-CASCI-QM/MM method with direct nonadiabatic dynamics techniques, including both surface hopping and multiple spawning. The new FOMO-CASCI-QM/MM method is applied to the photodynamics of the Green Fluorescent Protein fluorophore in vacuum, aqueous, and protein environments. The results allow us to understand why the fluorophore exhibits its peculiar fluorescence only when embedded in the protein environment.

PHYS 33 [631431]: Modeling reactive chemistry in protein active sites via mixed quantum mechanics/molecular mechanics methods

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We have developed mixed quantum mechanics/molecular mechanics (QM/MM) methods specifically designed to model reactive chemistry in protein active sites. The methodology will briefly be reviewed, followed by applications, using ab initio DFT methods for the QM region, to a wide range of proteins including methane monooxygenase, cytochrome P450, and triose phosphate isomerase. Quantitative agreement with experiment for structures, thermodynamics, and kinetics will be emphasized; typical errors obtained to date over a wide range of systems are on the order of a few kcal/mole.

PHYS 34 [644669]: Reactions of relevance to biological systems

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Abstract text not available.

PHYS 35 [637261]: Bond breaking and bond making in photobiology: Structure of the excited state force field of retinal chromophores

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Computational studies on different models of the 11-cis retinal chromophore (PSB11) of rhodopsin (i.e. the human retina visual pigment) indicate that a correct description of the geometrical and electronic structure of these chromophores can be achieved using an ab initio CASPT2//CASSCF/6-31G* level of theory (i.e. CASSCF geometry optimization and CASPT2 energy evaluation). Here we show that the same strategy can be used to investigate the factors responsible for the ca. 150 fs excited state (S1) lifetime observed in rhodopsin. Indeed, comparison of the S1 reaction path for the native chromophore and: (1) reduced chromophores, (2) locked chromophores and (3) counterion-chromophore pairs, give an unprecedented description of the sensitivity of retinal to intramolecular and environmental factors. Most importantly, we show that the QM/MM scheme CASPT2//CASSCF/AMBER allows for the evaluation of the equilibrium structure and excited-state properties and relaxation in the protein environment.



PHYS 36 [644201]: Solvation dynamics in protein environments

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A simple inhomogeneous model of protein dielectric properties will be discussed. A protein in solution is modelled as a collection of polarizable dipoles in a cavity embedded inside a dielectric medium. The intrinsic polarizabilities of 20 amino acids are assumed to be portable to all proteins in nature. A reasonable set of these polarizability values has been obtained by comparing dielectric fluctuations from molecular dynamics simulations with model calculations. The results are consistent within a data set of three small proteins. In order to validate the model ultra-fast laser spectroscopy experiments are performed for a chromophore in various mutants of myoglobin. The comparison between theory and experiments will be discussed.

PHYS 37 [644663]: Development of nonadiabatic molecular theory for simultaneous determination of nuclear and electronic wave functions: ab initio NOMO theory

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We have developed a simultaneous determination method of nuclear and electronic wave functions without the Born-Oppenheimer (BO) approximation, which is termed as ab initio NOMO theory. The Hartree-Fock (HF) equations have been derived for the nuclear orbital (NO), which is one-nucleus wave function, and the electronic molecular orbital (MO). Many-body effects have been examined and found that the electron-nucleus correlations are very important in our treatment. The separation of vibrational motion from the translational and rotational ones is also important in case adopting the Gaussian basis functions for the NOs. To represent the vibrational and electronic excited states, we applied the configuration interaction (CI) method to the NOMO theory.

PHYS 87 [636616]: Doing chemistry with MCSCF wavefunctions

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The primary driving force behind several decades of work on MCSCF methods has been this wavefunction's utility in describing chemical reactions including bond breaking. However, bond breaking is just one example of electron unpairing/re-pairing, and indeed MCSCF wavefunctions are also useful for the description of excited states or ionization processes. A number of technical improvements to programs for the generation of MCSCF wavefunctions

will be presented, including scalable integral transformations, improved CI methodology permitting increasingly larger active spaces, strategies for orbital optimization, and treatments for dynamic correlation. Some speculation about future progress will be given. Although MCSCF's success in treating reactive channels is well known, this method also provides useful chemical interpretations. Indeed, it is one of the strong points of MCSCF that it involves an active space, allowing one to focus attention on the reacting electrons and the shapes of the orbitals that hold them. Orbital invariance within the active space (and within the doubly occupied space) permits localized or natural orbital generation. Expressing the wavefunction in terms of the former, in particular, leads to a great deal of chemical insight into bonding patterns. This will be demonstrated by examples drawn from previous and current research using MCSCF methods.

PHYS 88 [643518]: Assessing quantum chemical methods for bond breaking: Single-reference, multi-reference, and minimalist models

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Various single- and multi-reference methods have been evaluated for their performance in bond breaking reactions by comparing to full configuration interaction potential energy curves, which represent the exact solution of the electronic Schrodinger equation for a given one-particle basis set. Even in the simplest case of breaking a bond to a hydrogen atom, the best unrestricted single-reference method in common use, UCCSD(T), exhibits nonparallelity errors of about 3 kcal/mol. Available multi-reference methods provide significant improvement, although at the price of increased complexity and computational cost. New, minimalist models of bond breaking in a generalized restricted active space configuration interaction (RAS CI) framework will be described, and various choices of orbitals for both single- and multi-reference approaches have been explored. Finally, different basis sets have been compared for their performance in full configuration interaction benchmarking, and natural orbitals are found to dramatically improve predictions of molecular properties.

PHYS 89 [642106]: Direct CI and MCSCF method for multiple active spaces with variable occupations

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In order to reduce the number of ineffective configurations in a priori generated configuration spaces, a direct configuration interaction (CI) method has been developed which limits the electron occupations of orbital groups making up a total active space. A wavefunction is specified by firstly partitioning an active space into an unrestricted number of orbital groups and secondly by providing limiting values, in the form of minima and maxima, for the electron occupancies of each group. The CI problem corresponding to all possible determinants satisfying these conditions is solved in a fully direct manner by the use of Slater-Condon expressions in conjunction with single and double replacements. This CI approach, termed Occupation Restricted Multiple Active Space-CI (ORMAS-CI), has also been linked with orbital optimization programs to produce the ORMAS-SCF method. Several applications will be presented demonstrating that large CI spaces may be drastically reduced with negligible loss of accuracy.

PHYS 90 [636419]: String product space self-consistent field method and second-order perturbation theory

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A multiconfiguration self-consistent field (SCF) method is presented where the string product space (SPS), the product space of alpha- and beta-string spaces, is used as a variational space. The computational effort for wavefunctions is significantly reduced compared with the complete active space self-consistent field (CAS-SCF) method, and yet the accuracy is comparable to the CAS-SCF case. A computational scheme and some numerical examples for potential energy surfaces and excitation energies are shown. Furthermore, a multiconfigurational quasi-degenerate perturbation theory (MC-QDPT) [Nakano, J. Chem. Phys., 99, 7983 (1993)] using the SPS-SCF reference wavefunctions is also presented. The inclusion of dynamic correlation by the second-order MC-QDPT scheme fairly improves the SPS-SCF results, giving chemical accuracy.

PHYS 91 [643594]: Large full valence spaces without configurational deadwood

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Molecular electronic structures are described by wavefunctions consisting of (i) zeroth-order terms (SCF or MCSCF) and (ii) refinement terms (accounting for dynamic correlation). In most systems, the fundamental understanding of bond forming and breaking as well as reaction paths emerges from the zeroth-order terms. A classical and effective zeroth-order choice is the optimized full valence-space of deformed minimal-basis atomic orbitals. While even this limited configuration space grows too large for practical use in moderately sized molecules, its growth is largely due to vast increasing amounts of ineffective configurations. We have developed a systematic procedure for eliminating a-priori all configurational deadwood and thereby reducing the configurational expansion by orders of magnitude. The reduction fraction moreover increases with the size of the molecule, making larger systems accessible. In this context, we have shown CI expansions generated from split-localized orbitals to converge faster than those generated from natural orbitals.

PHYS 114 [643851]: Equation of motion coupled-cluster methods and multireference issues

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It may not be widely appreciated that equation-of-motion coupled-cluster (EOM-CC) methods have many of the same advantageous features usually associated only with strictly multiconfigurational approaches such as MCSCF, MRCI, MR-CEPA etc. These formal features of EOM-CC make it superior to traditional CC methods even for some problems in which the latter could be applied. The treatment of multireference problems with EOM-CC methods will be discussed, and illustrated by some applications to radicals. Finally, the extent to which these methods can be used to treat bond-breaking in polyatomic molecules will be surveyed.

PHYS 115 [637188]: Describing new chemistry by the spin-flip method: Electronic structure and thermochemistry of the dehydro-meta-xylylene triradical

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The spin-flip (SF) approach allows one to describe multi-configurational wave functions within a single reference formalism. Technically, SF employs a high-spin state as a reference and treats the target low-spin states as spin-flipping excitations from the reference state. Using the SF approach, one can extend the single-reference models such as HF, MP2, or CCSD to describe bond-breaking, diradicals and triradicals. This work discusses the electronic structure of the dehydro-meta-xylylene (DMX) triradical which has two pi and one sigma unpaired electrons. We found that the ground state of this molecule is an open-shell doublet, in agreement with recent experimental studies [Munsch and Wenthold], the quartet state being 0.1-0.3 eV higher in energy. The calculated triradical separation energies are consistent with experimental data and demonstrate considerable interaction between sigma and pi systems.

PHYS 116 [641455]: Single- and multi-reference coupled-cluster methods for quasidegenerate electronic states and bond breaking

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Accurate calculations of quasidegenerate electronic states and molecular potential energy surfaces involving bond breaking represent a particularly challenging problem for ab initio methods. The most natural approaches to this problem are based on the multi-reference description. Thus, we will discuss new classes of genuine and state-specific (or active-space) multi-reference coupled-cluster methods, developed by our group, that can be used in studies of bond breaking and excited electronic states. One can also try to redesign the existing single-reference coupled-cluster methods, so that they can be applied to bond breaking and quasidegenerate and excited states with the ease-of-use of the single-reference theory. We have made progress in this area by developing the renormalized, quadratic, and extended coupled-cluster methods. All those methods will be discussed. The excited-state extensions of the renormalized coupled-cluster methods will be described by Dr. Karol Kowalski in his presentation.

PHYS 117 [642198]: Breaking bonds perturbatively

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This talk will present our work on developing perturbative corrections to coupled-cluster theory appropriate for describing bond breaking. We start by dividing the similarity-transformed Hamiltonian $e^{-T}He^T$ into zeroth- and first-order pieces. Based on this partitioning we derive a second-order correction to the coupled-cluster energy. Starting with a coupled-cluster singles and doubles (CCSD) wave function yields a correction containing both triple and quadruple excitations. We will present results for the ensuing CCSD(2) method, as well as for methods based on CCSD variants designed to handle both very difficult [QCCD(2)] and very large [PP(2)] systems.

PHYS 118 [640538]: New class of noniterative energy corrections to coupled-cluster energies for excited electronic states

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Equation-of-motion coupled-cluster theory with singles and doubles (EOMCCSD) has been successful in describing the excited states dominated by single excitations, but it fails to describe states that have significant doubly excited components and excited-state potential energy surfaces (PESs). To alleviate this problem, we have recently combined the EOMCC theory with the method of moments of coupled-cluster equations. This allowed us to introduce new types of noniterative energy corrections to EOMCCSD energies defining the renormalized EOMCCSD(T) approaches which are as easy to use as the standard CCSD(T) ground-state method and which provide spectacular improvements in the description of excited-state PESs and excited states dominated by two-electron transitions. Preliminary results for the ozone and other benchmark molecules (CH⁺, HF, C₂, N₂, MnO₄⁻, etc.), indicate that the single-reference renormalized EOMCCSD(T) method may successfully compete with the expensive and a lot more complicated multireference approaches.

PHYS 143 [648191]: Coupled-cluster methods and their applications to energetic molecules

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Several recent developments in coupled-cluster methods are described. These include highly accurate results that involve connected quadruple and pentuple excitations, and their non-iterative counterparts. We also consider excited states at the EOM-CCSDT level and beyond. Applications to prototype energetic molecules will include (NO)₂, which like ozone poses severe difficulties quantum chemical methods; and the nitramines, H₂N-NO₂ and its methyl and dimethyl forms. The latter are of interest in bi-molecular versus unimolecular decomposition which should be a defining characteristic of condensed phase reactions.

PHYS 144 [638634]: Multireference coupled cluster methods and local correlation

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Local correlation treatments are known to be highly effective as a means to include dynamical (short-range) correlation effects for larger molecules. In addition, localized orbitals are very suitable to describe the breaking and formation of chemical bonds, as they hardly change character in the process. Suitable active spaces in multireference treatments of potential energy surfaces can therefore be most conveniently expressed in terms of localized orbitals. Likewise, configuration selection, which is necessary for Multireference calculations using larger active spaces, is most robust in a local representation. In this talk, I will explore the use of truncated CC approaches of both the single and multireference type in a local basis. These results have been obtained using automatically generated computer codes, and I will comment briefly on our progress in automatic synthesis of state-of-the-art electronic structure programs.

PHYS 145 [643766]: Fast methods for electron correlation

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Density functional theory (DFT) has become the method of choice for routine applications of electronic structure theory because it offers the best tradeoff between accuracy and feasibility. However, for some applications, such as reliable description of potential surfaces for bond-breaking, or obtaining high accuracy, present-day DFT remains inadequate. Many-body wavefunction-based approaches offer an attractive, systematically improvable alternative, but suffer from computational costs that increase much more steeply with molecular size than DFT. In this talk, recent developments towards formulating "fast" many-body methods will be discussed, based on the fact that electron correlation is primarily a local phenomenon. The performance of these methods for breaking chemical bonds, and other applications, will be assessed.

PHYS 146 [640337]: Local coupled cluster methods for molecular response properties

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For ground-state wave functions and energies, local correlation methods have successfully overcome the polynomial scaling wall of high-accuracy ab initio models such as coupled cluster theory. However, to date the development of local schemes for molecular *properties* has been limited. This talk will focus on our recent efforts to extend local coupled cluster methods to linear-response properties of large molecules, including excitation energies and dipole polarizabilities (in both the static and dynamic limits). The talk will include recent results using "standard" local-domain schemes as well as more recently developed methods that are applicable to bond-breaking regions of the potential surface.

PHYS 147 [644916]: Equation-of-motion spin-flip coupled-cluster model with single and double substitutions: Theory and application to sigma-pi diradicals

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A new electronic structure method, equation-of-motion spin-flip coupled-cluster model with single and double substitutions (EOM-SF-CCSD), is presented. Formal relationships between the EOM-SF-CCSD and traditional (non-SF) EOM-CCSD method for excitation energies (EOM-EE-CCSD) are discussed. The importance of orbital relaxation effects is demonstrated by comparing the EOM-SF-CCSD model with the EOM-SF optimized orbitals CCD results. Results for ortho-, meta-, and para-didehydrotoluene are presented.

PHYS 200 [640890]: Breaking chemical bonds in molecules and crystals: Methods and physical insight

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The first part of the talk will focus on recent advances in reduced scaling local correlation methods for molecules. These include local multireference single and double excitation configuration interaction (MRSDCI) and local average coupled pair functional methods that allow size extensivity errors to be corrected for. We demonstrate dramatic reductions in scaling while retaining chemical accuracy. In the second part of the talk, we will discuss how bonds break in crystals. We propose a simple universal law that describes how a crack forms in a crystal and demonstrate its universality via periodic density functional theory calculations on three disparate materials: a metal, an oxide ceramic, and a semiconductor. *In collaboration with A. Venkatnathan, R. Gdanitz, A. Szilva, D. Walter, R. L. Hayes, and M. Ortiz. This work was funded by the NSF and the DOD-MURI program.

PHYS 201 [643606]: Bond breaking and formation in the reaction of acetylene on the Si(100)-(2x1) surface

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We have examined the reaction of acetylene with the Si(100)-(2x1) surface using a Fully Optimized Reaction Space – SCF wavefunction. This surface is characterized by rows of silicon dimers. Acetylene reacts with these dimers. The bare surface is highly multi-reference due to partial π bonding in the silicon dimers. We have looked at several

minima on the surface and the pathways between them. These isomerizations involve the making and breaking of carbon-carbon and silicon-silicon pi bonds, and carbon-silicon sigma bonds. Some of the minima on the surface and nearly all of the associated transition states have significant partial orbital occupations. Because of these partial occupations, it is important to use multi-reference methods to accurately study this potential energy surface and those of similar systems. This reaction is one example of the wider class of molecules reacting on Si(100)-(2x1). When studying these phenomena it is essential that a multi-reference method be used.

PHYS 202 [638693]: Theoretical studies of chemical reactions following electronic excitation

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The use of multi-configurational wave functions is demonstrated for several processes: tautomerization reactions in the ground and excited states of the DNA base adenine, dissociation of glycine molecule after electronic excitation, and decomposition/formation of novel rare gas molecules HRgF. These processes involve bond breaking/formation and require multi-configurational approaches that include dynamic correlation.

PHYS 203 [643393]: Investigation of hydrogen transfer reactions with the multiconfigurational nuclear-electronic orbital method

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Applications of the nuclear-electronic orbital (NEO) method to hydrogen transfer reactions will be presented. In the NEO method, both electronic and nuclear molecular orbitals are expressed as linear combinations of Gaussian basis functions, and the variational method is utilized to minimize the energy with respect to all molecular orbitals. The centers of the nuclear basis functions are also optimized variationally. Significant correlation effects are included using a multiconfigurational self-consistent-field approach. Analytic gradients allow for geometry optimizations and the generation of minimum energy paths and dynamic reaction paths. For hydrogen transfer reactions, the transferring hydrogen nuclei, as well as all electrons, are treated quantum mechanically to include nuclear quantum effects such as zero point energy and hydrogen tunneling. In this case, the reaction coordinate depends explicitly on only the classical nuclei, and the imaginary mode at the transition state corresponds to heavy-atom motion that drives the charge transfer reaction via reorganization.

PHYS 204 [644629]: Dissociation of oxygen and water at metal oxide surfaces: Role of the surface and surrounding environment

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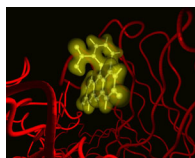
Metal oxide surfaces are important in a wide range of technological applications such as catalysis, microelectronics, gas sensing, and corrosion protection. The growth, structure, and subsequent performance of these surfaces are very sensitive to the partial pressures of oxygen and water present in the environment. Hence understanding how dissociation of oxygen and water at surfaces depends upon the type of metal oxide and concentration of reactants is key for predicting and controlling performance of these materials. Results from both density-functional and wavefunction-based methods applied to clusters and periodic systems will be presented.

PHYS 437 [640042]: From molecules to proteins: Possibilities for data and algorithmic integration using HPC technologies

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To deepen our understanding of natural and synthetic processes and to support current experimental progress, there is an increasing need for affordable theoretical calculations of chemical reactions in complex systems like solutions, biomolecules and materials. Intricacies of dynamical motion in protein and enzymatic systems, mechanistic aspects of biochemical reaction processes in solution, and determination of key dielectric phenomenon all require careful use of methodology if accurate and reliable results are to be expected. In the last few years, many efforts have been undertaken to combine techniques involving quantum mechanics with other less expensive approaches, most

notoriously, QM/MM. This presentation will focus on strategies for hybrid techniques that are being developed in this group, based on algorithmic modifications and extensions to our quantum mechanical approach for the inclusion of solvent effects, COSab. Features of the methods will be highlighted using several examples of calculations performed on biochemical systems of interest.



PHYS 438 [639142]: Artificial intelligence for electronic structures: Automated parallel implementations of configuration-interaction, coupled-cluster, and many-body perturbation theories

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Many-electron theory offers a variety of converging approximations to tackle chemical problems including bond breaking and formation. However, such studies are often deterred not only by limited computational resources but to a greater extent by the complexity of the process of deriving the working equations and implementing efficient programs of the approximations, which can even take man-years of efforts. We present a symbolic manipulation program that abstracts and automates the derivation and parallel implementations of second-quantized models of many-electron theory and its applications to parallel implementations of CI up to CISDTQ, CC up to CCSDTQ, and non-canonical MBPT up to fourth order. These computer-generated programs fully take advantage of spin, spatial, and index permutation symmetry, adjust memory usage by tiling algorithm, and balance parallel workload dynamically, and can compete with carefully hand-coded programs in performance.

PHYS 439 [642702]: Parallel multiconfigurational self-consistent field

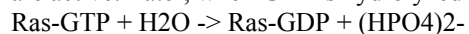
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A distributed data multiconfigurational self-consistent field (MCSCF) algorithm based on the full Newton-Raphson orbital update method, with an augmented Hessian, is presented. Scalability up to 512 processors is demonstrated. Application is made to the fragmentation of guanine (a basic component of DNA) under electron attachment.

PHYS 440 [645641]: Bond dissociations associated with GTP hydrolysis

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GTP-binding proteins (GTPases) play an important role in a variety of biological processes such as cell growth control and control of transcription. Particularly, the Ras family proteins of GTPases play an important role in linking receptors on the plasma membrane to signaling pathways. Ras mutants, which are found in 25-30% of human tumors, are believed to encourage uncontrolled cell growth. When GTPases are bound to GTP these proteins are active. Later, when GTP is hydrolyzed to GDP, these proteins become inactive:



The hydrolysis can be catalyzed by GTPase-activating proteins. In spite of the obvious importance of GTP hydrolysis, the mechanism is still controversial. We will present bond dissociation energies and other thermodynamic properties for GDP, GTP, Ras-GTP, and other related chemical compounds.

PHYS 441 [640461]: Analytic energy second derivatives for MCSCF wavefunctions: Implementation and parallelization

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MCSCF techniques are widely used in describing bond breaking due to the inherent multiconfigurational nature of the process. Analytic MCSCF energy gradients have seen widespread use in characterizing stationary points on electronic potential energy surfaces, due to their superiority in both accuracy and efficiency over their numerical

counterparts. Use of analytic MCSCF second derivatives, however, has been severely limited due to increased complexity and computational demands required to generate such quantities. Analytic second derivatives for the determinant-based complete active-space variant of MCSCF have been recently implemented into GAMESS. General aspects of the current implementation will be discussed. A more detailed analysis of issues pertaining to parallelization will also be presented.

PHYS 465 [641896]: Electron correlation treated using time-dependent approaches

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Electron correlation in molecules can be described using time dependent methods. We will discuss two approaches. First, the use of auxiliary fields to replace electron-electron interactions will be discussed. This method will be shown to yield very highly accurate electronic energies in molecules. We will next discuss how correlation over time should be incorporated into time dependent density functional theory. This can be elegantly done via functionals that depend on the current density. The non-adiabatic part of the electron correlation is rigorously manifested in a transverse vector potential. This is then a "exchange-correlation magnetic field" which is always present even when there is no real magnetic field in the problem.

PHYS 466 [643192]: Can density functional theory provide a reliable description of bond making/breaking processes?

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DFT is presently the only method, which can reasonably describe chemical processes involving large molecules at acceptable cost. Nevertheless, there are also many examples of its failure: Reaction barriers are underestimated, false intermediates are predicted or an erroneous asymptotic behavior for bond dissociation is calculated. It is shown that pitfalls and shortcomings of DFT can be avoided by an educated use of the method. This implies careful handling of the self-interaction error of approximate XC-functionals or the suppression of a double counting of non-dynamic electron correlation when using multi-reference DFT. For the purpose of assessing the performance of DFT more clearly, the detailed mechanism of bond making / breaking processes is discussed.

PHYS 467 [638732]: The spin-flip approach within time-dependent density functional theory

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Krylov's spin-flip approach is extended from wavefunction based methods to density functional theory framework. This extension naturally combines the strengths of both the spin-flip approach, which is suitable for describing non-dynamical correlation, and density functional theory, which well accounts for dynamical correlation. This new method (SF-DFT) is implemented within the Tamm-Dancoff approximation to the time-dependent density functional theory within the Q-Chem electronic structure software package. We will present some results on bond-breaking, diradicals, and other interesting problems.

PHYS 468 [651120]: Excited states via linear response in DFT and HF free of basis set error

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We will describe the computation of excitation energies and transition densities using multiresolution in multiwavelet bases. These results, for general polyatomic systems, are free of basis set error (more precisely have guaranteed precision) and are compared with computations in conventional atom-centered Gaussian bases.

PHYS 469 [644556]: Bond-breaking in density functional theory

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We review the basic difficulties of bond-breaking within KS density functional theory, using H₂ as the canonical example. We will discuss why spin-contamination of KS wavefunctions is a good thing, if correctly interpreted. We will discuss recent work on RPA calculations of ground-state energies, corrected by either TDDFT or short-range GGA, showing how such calculations correctly dissociate.