Abstract:

The goal of this project is to apply powerful new simulation techniques to tackle computationally challenging problems in chemical dynamics, with special emphasis on electrochemistry, heterogeneous catalysis, nanoparticles, solid-state dynamics, and photochemistry. These calculations are being carried out in part with new high-throughput integrated software that we are developing. New research capabilities in computational chemical dynamics are expected to play a significant role in enabling environmental scientists worldwide to address environmental challenges facing DOE and the nation. Recent advances in computer power and algorithms have made possible accurate calculations of many chemical properties for both equilibria and kinetics. Nonetheless, applications to complex chemical systems, such as reactive processes in the condensed phase, remain problematic due to the lack of a seamless integration of computational methods that allow modern quantum electronic structure calculations to be combined with state-of-the-art methods for chemical thermodynamics and reactive dynamics. These problems are often exacerbated by unvalidated methods and limited software reliability. Our consortium is developing an integrated software suite that combines electronic structure packages with dynamics codes and efficient sampling algorithms for the following kinds of condensed-phase modeling problems that we propose to tackle in various parts of the present Grand Challenge project: thermochemical kinetics and rate constants, photochemistry and spectroscopy, chemical and phase equilibria, electrochemistry, and heterogeneous catalysis. These fundamental areas of research are important for solar energy, fuel-cell technology, environmental remediation, weather modeling, pollution modeling, and atmospheric chemistry. Photochemical creation of excited states offers a means to control chemical transformations because different wavelengths of light can be used to create different vibronic states, thereby directing chemical reactions along different pathways. It is crucial to understand how energy deposited into the system is used; this is particularly complicated in condensed phase systems where there are many ways to dissipate excess energy. Similar opportunities and challenges present themselves in the areas of electrochemistry and catalysis. We therefore propose to carry out prototype large-scale applications on environmental problems as well as other applications to complex chemical dynamics processes, focusing on three high-impact areas. In the computational electrochemistry area, we are especially concerned with processes that enhance the design of fuel cell technology. For heterogeneous, nanoparticle, and solid-state dynamics, we are developing an array of methods for multi-time-scale simulation of nucleation of crystals in solution, reactions of radicals in solution, zeolite catalysis, structure and dynamics of gallazane precursors to gallium nitride nanocrystals, the regulatory role of metal ions in the reactivity of inorganic phosphates, nanoparticles structure, and ice dynamics. In the computational photochemistry area, we are constructing potential energy surfaces for a number of photochemical reactions and employing them for dynamics calculations based on the new decay of mixing with coherent switches algorithm. If time permits, we will also consider solvatochromic shifts on conical intersections that govern selected photo chemical processes.
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Number of CPU-hours allocated for FY2008
1,050,000

Number of CPU-hours actually used for FY2008
829,438

Number of CPU-hours requested for FY2009
800,000
Overview of the accomplishments and activities in FY2008

1. Use of Minnesota density functionals in studying supramolecular compounds
(Yan Zhao and Donald G. Truhlar)

One of the most vigorously developing technological research areas is the field of supramolecular chemistry, which involves the use of noncovalent interactions to assemble molecules into stable, well-defined structures called supramolecules. Most of the experimental studies of supramolecular selfassembly are carried out in the condensed phase since the gas-phase supramolecular experiments are technically too demanding; however, theoretical and computational studies can be more reliably carried out for gas-phase supramolecular systems, and such theoretical studies can shed light on intrinsic supramolecular structures and energetics, thus complementing the experimental investigations. One promising approach is density functional theory, which has an excellent performance-to-cost ratio. However, the popular B3LYP density functional and most other older functionals are inaccurate for noncovalent (for instance, aromatic-aromatic) interactions. One of the ways to improve the performance of DFT is to optimize the exchange-correlation functionals for a broad range of properties including rare-gas dimers, aromatic-aromatic interactions, and other data sensitive to medium-range correlation energy, such as barrier heights. This approach has been used for the development of the M06-2X density functional which has been validated for \( \pi \ldots \pi \) stacking and has also been employed to study supramolecular assembly involving a nanoring and to study the dimerization of coronene as a model for interacting graphene sheets in multiwalled carbon-based assemblies.

One of the most exciting topics of the project is an application of the Minnesota density functionals (M06-L and M06-2X) to study the geometries and binding energies of a recently synthesized tweezers-like buckyball catcher (C\(_{60}\)H\(_{28}\)) and its supramolecular complexes with buckminsterfullerene C\(_{60}\) (see the figure). The C\(_{60}\)H\(_{28}\) buckycatcher has two corannulene pincers and a tetrabenzo-cyclooctatetraene tether. The C\(_{60}@C\(_{60}\)H\(_{28}\) supramolecule is bound by the strong attractive concave-convex aromatic-aromatic interactions between the corannulene pincers and the C\(_{60}\) molecule. However, due to the entropy penalty, the calculated gas-phase free energy of association of the C\(_{60}@\)corannulene supramolecule is positive 3.5 kcal/mol; and this entropy penalty explains why it is difficult to observe such C\(_{60}@\)corannulene supramolecules experimentally.

We have also been using coronene dimers as prototypes for graphene material simulation. Graphene sheets are the building blocks of carbon nanotubes and a variety of functionalized nanomaterials. Methods to be used for computer-aided design of such materials or for the study of aromatic-aromatic interactions in biopolymers and other soft materials should be validated for smaller systems where reliable estimates of interaction energies are available. In our work, we first validated the M06-2X functional against the S22 database of noncovalent interaction...
energies of biological importance. We then applied the M06-2X functional to study aromatic-aromatic interactions in coronene dimers. We located six stationary points on the potential energy surface of coronene dimer, we calculated the potential energy curves for the sandwich, T-shaped, and parallel-displaced configurations of this prototype of aromatic-aromatic interactions, and we found that a parallel displaced configuration is the global minimum. The potential curves for the coronene dimers will aid the development of new force fields and potential energy functions that are computationally efficient and capable of modeling large graphene or aromatic clusters.
We have obtained benchmark binding energies for five zeolite model complexes, with four of the adsorbates bound noncovalently and one covalently. The binding energies were determined as the sum of the infinite-basis-set limit of Møller-Plesset second-order perturbation theory (MP2) energies and a CCSD(T) correction term evaluated with the aug-cc-pVDZ basis set. The basis set limit of MP2 energies was determined by two-point extrapolation using the aug-cc-pV\(X\)\(Z\) basis sets for \(X = D\) and \(T\) and separate extrapolation of the Hartree-Fock and correlation energies. We found that correlation contributions beyond MP2 to the final binding energies are small; their magnitude is in the range of 0.02-1.0 kcal/mol. For the MP2 method to describe the interactions in these zeolite model systems accurately, one needs to use a basis set at least the size of aug-cc-pVTZ in conjunction with counterpoise corrections. Final binding energies of the model complexes are in the range of 3.5-19.5 kcal/mol, and they were used as reference data to test 6 wave function methods and 41 density functionals. Among the tested density functional methods, M06-L/6-31+G(d,p) gives a mean unsigned error (MUE) without counterpoise correction of 0.87 kcal/mol. With counterpoise corrections, the M06-2X and M05-2X functionals give the best performance. The MUE with counterpoise corrections for the M06-2X/6-311+G(2df,2p)//MP2/6-311+G(2df,2p) level of theory is 0.39 kcal/mol. With the DFT/6-31+G(d,p) geometries and the 6-311+G(2df,2p) basis set, M05-2X and M06-2X give MUEs with counterpoise corrections of 0.40 and 0.52 kcal/mol, respectively. Tests against the binding energies of four complexes (two noncovalent and two covalent) of the adsorption of isobutene on a large 16T zeolite model cluster confirmed that M06-L, M06, M05-2X, and M06-2X are very promising quantum mechanical methods for hybrid quantum mechanical/molecular mechanical (QM/MM) simulations of zeolites. In fact the performance of these four Minnesota functionals, as compared to other high-quality functionals, is relatively even better for the larger 16T clusters than for the smaller 3T ones.
3. Modeling of solvation effects (Aleksandr V. Marenich, Christopher J. Cramer, and Donald G. Truhlar)

We have developed a new charge-density based solvation model called SMD. The SMD algorithm involves an integration of the nonhomogeneous Poisson equation for electrostatics. The SMD model has been parametrized using a large training set of neutral and ionic solvation free energies for various solutes in water and organic solvents (nearly 3000 data). The non-bulk-electrostatic part of the SMD model utilizes the cavity–dispersion–solvent-structure formalism that was worked out for previous solvation models developed at the University of Minnesota.

The SMD model parameters are recommended to be used for the calculation of solvation free energies within the frameworks of the Polarizable Continuum Models implemented in Gaussian 03 and GAMESS, and it can be used in conjunction with the Generalized Conductor-like Screening Model (GCOSMO) implemented in NWChem. (Note that NWChem calculations were performed at the EMSL computing facilities whereas Gaussian and GAMESS calculations were carried out at the Minnesota Supercomputing Institute facilities.)

The figure below demonstrates the significant improvement in the quality of IEFPCM/Gaussian 03, CPCM/GAMESS, and GCOSMO/NWChem upon using the SMD parameters instead of the default settings for the current implementations of these models in Gaussian 03 (G03), GAMESS, and NWChem (note: MUE stands for mean unsigned error, that is, mean absolute deviation from a set of accurate data).

The new SMD model will complement the recent SM8 model based on the generalized Born equation for electrostatics.
4. Large-scale parallel calculations with combined coupled cluster and molecular mechanics formalism: excitation energies of zinc-porphyrin in aqueous solution
(Peng-Dong Fan, Marat Valiev, and Karol Kowalski)

Zinc-porphyrin (ZnP) is important in understanding photochemical properties of π-conjugated systems. Vertical excitation energies of ZnP monomer was previously studied by SAC-CI method and TD-DFT method. However, due to the size of the system (consisting 37 atoms and 190 electrons), the high order correlation effects (e.g. triply excited configurations) still remain unknown. The environment effect on the excited states of ZnP have not been studied either.

To address the above issues and demonstrate the performance of our parallel codes, we performed cutting edge large scale benchmark excited state calculations of ZnP monomer in aqueous solution using combined coupled cluster molecular mechanics formalism, in which the coupled cluster (CC) methods are equation of motion approach with singles and doubles (EOMCCSD) and completely renormalized non-iterative triples corrections to EOMCCSD method (CR-EOMCCSD(T)).

The calculations show that the non-iterative triples corrections ranges from 0.24 eV to 0.29 eV, and the CC approaches provide consistent energetics of low-lying excited states for all environments, while the TD-DFT approach can not adequately describe prototype charge transfer states dominated by excitations from central zinc and nitrogen atoms to carbon atoms. Such breakdown of TD-DFT is best observed in aqueous environment. The parallel performance of our code scales cross 1000 CPUs. The scalability is 1.92 and 1.94 for the CCSD and EOMCCSD methods, respectively, when going from 256 CPUs to 512 CPUs, and 1.66 and 1.74, respectively, from 512 CPUs to 1024 CPUs.

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5. Calculation of reaction rates for barrierless association reactions using variational transition theory (Jingjing Zheng and Donald G. Truhlar)

This project is focused on calculations of quantitatively accurate reaction rate for barrierless association reactions by means of variational transition state theory. One of the challenges for predicting accurate reaction rates of barrierless association reactions is to calculate accurate potential energy surface in the transition state regions. The difficulty is due to the large multireference character in the bond-forming regions.

The investigated association reactions are CN + NH$_3$ and OH + SO$_2$. High level \textit{ab initio} methods, e.g. CCSDT and CCSDTQ with augmented tripe zeta basis sets, were used to generate accurate minimum reaction path for radical-radical association reactions. Although these high level calculations may give accurate potential energy surfaces, they are not affordable for dynamics calculations. Therefore, these high-level potential energy surfaces are used to validate density functional calculations. By comparing various density functional calculations with these accurate potential energy surfaces, we can select a proper combination of density functional and basis set for direct dynamics calculations.
6. Investigation of hydrous silica melts
(Kelly E. Anderson, Katie A. Maerzke, J. Ilja Siepmann, and Christopher J. Mundy)

Understanding the structure of hydrous silica (SiO$_2$) melts is important for gaining insight into the structure of the Earth’s upper mantle. Pressures within the mantle range from 1 GPa to 135 GPa at the core-mantle boundary and temperatures range from several hundred to a few thousand Kelvin. This wide range of combined high temperatures and pressures makes experimental studies of these systems challenging. Simulation provides an alternative means to examine structural properties. Previously, our group used an empirical force field to examine hydrous silica melts at high temperatures and moderate pressures (0.25-10 GPa) using Monte Carlo (MC) simulations in the isobaric-isothermal ensemble.\(^1\)

We have sought to probe these systems via first-principles molecular dynamics (FPMD) simulations using Kohn-Sham density functional theory to represent the interactions. These simulations were performed under isobaric-isothermal conditions using the CP2K simulation package and the Gaussian plane wave method implemented therein\(^2\) to calculate energies and forces. The BLYP functional was used in conjunction with the Goedecker-Teter-Hutter pseudo-potentials and a Gaussian double-$\zeta$ valence basis set and a charge density cutoff at 280 Ry. The lengths of the trajectories were 50 ps with a time step of 0.5 fs. The last 80% of the trajectory was analyzed. Analysis of both the MC and FPMD simulations shows that more than 95% of Si atoms have at least three O nearest neighbors ($r_{\text{SiO}} \leq 2.35$ Å; taken from the minimum of the radial distribution function). In the absence of water, the silica melt forms a highly networked liquid. The addition of even relatively small amounts of water (3.2 wt.%) is sufficient to substantially change the structure of the liquid. A more detailed analysis of the first principles simulations is being prepared for publication.

Katie Maerzke participated in PNNL’s 2008 Summer Research Institute.

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7. Molecular dynamics simulation for the transport of ions through the phospholamban membranes (Alessandro Cembran and Jiali Gao)

Phospholamban (PLN) is a single pass membrane protein that reversibly binds and regulates the sarcoplasmic reticulum (SR) Ca$^{2+}$-ATPase (SERCA). The SERCA/PLN complex is responsible for Ca$^{2+}$ ions transport from the cytoplasm into the SR lumen, causing muscle relaxation. PLN exists in equilibrium between the pentameric and monomeric forms, and it is the monomeric form that is the active, inhibitory species, regulating Ca$^{2+}$ transport. However, the function of the oligomeric configuration has puzzled biochemists and biophysicists for many years, and literature suggests that it might act as a Cl$^{-}$ or Ca$^{2+}$ ion channel.

We computed through molecular dynamics (MD) simulations the potential of mean force (PMF) for the Cl$^{-}$ and Ca$^{2+}$ ion conduction through the PLN pentamer pore. We determined the barriers for the passage of Cl$^{-}$ and Ca$^{2+}$ to be 19 and 41 kcal/mol, respectively, values that are too high for the translocation to take place. This result, together with electrochemical measurements performed by collaborators, reinforced the hypothesis of PLN pentamer to be a storage form and not an ion channel.

The structure and dynamics of the monomeric and pentameric forms of PLN have also been investigated with molecular dynamics simulations. Specifically, our research focused on the structural and dynamical effects due to the protein interaction with the lipid bilayer. We compared our results to NMR data. We highlighted the different dynamics of the cytoplasmic loop when embedded at the membrane/water interface or when fully exposed to the solution.
Description of FY2009 proposed research

We will be working on the development and application of Feynman path integral methods that provide an excellent means of incorporating either approximate or exact quantum mechanical treatments into statistical thermochemistry calculations. Our objective is to develop and benchmark a number of more accurate and efficient approximation schemes that will permit treatment of larger systems and we will also be exploring more efficient sampling algorithms. A particular focus of future work will be the coupling of our methods to standard molecular dynamics programs so that quantum effects for key coordinates may be treated in biologically important systems. Another key interest is in developing schemes to efficiently treat anharmonic effects in molecular systems to improve the accuracy of transition state theory rate constant calculations.

We will continue our work on zeolite catalysis. It includes the development of new potential energy functions for the study of adsorption isotherms of hydrocarbons in zeolites. The new potential energy functions are based on a combined quantum mechanical/molecular mechanical method involving adaptive partitioning so that the zone treated quantum mechanically moves with the adsorbate. We are interfacing this new potential with a Monte Carlo Gibbs ensemble algorithm to calculate the adsorption isotherms.

We continue to incorporate our solvation models into user-friendly, portable, and well integrated software freely distributed by the University of Minnesota. This software is available at http://comp.chem.umn.edu. We plan to incorporate our new solvation model SMD into the NWChem computational package. Since the latest revision of NWChem includes the Minnesota suite of density functionals the integrated NWCHEMPLUS implementation of SMD will allow for exploration of a promising combination of the newest and most accurate (up-to-date) solvation model with the highly effective density functionals.
List of publications supported in part by this Computational Grand Challenge grant, 2007-2008


List of presentations, 2007-2008

“Density functionals with broad applicability for main group and transition metal chemistry, spectroscopy, kinetics, and noncovalent interactions,” D. G. Truhlar, Max T. Rogers Lecture Series, Michigan State University, Apr. 22, 2008.


List of significant methods, routines or codes

NWChemRate 2007 (Jingjing Zheng, Mark A. Iron, Benjamin A. Ellingson, José C. Corchado, Yao-Yuan Chuang, and Donald G. Truhlar)

NWChemRate is a set of FORTRAN subroutines and Unix scripts for interfacing the POLYRATE and NWChem computer programs for the purpose of carrying out direct dynamics calculations of gas-phase chemical reaction rates of polyatomic species (and also atoms and diatoms as special cases) using the electronic structure methods available in NWChem to calculate the potential energy surface and POLYRATE for the dynamics. The interface is based on the POLYRATE hooks protocol. The dynamical methods used are variational or conventional transition state theory and multidimensional semiclassical approximations for tunneling and nonclassical reflection. Rate constants may be calculated by any of the methods available in POLYRATE for canonical or microcanonical ensembles or for specific vibrational states of selected modes with translational, rotational, and other vibrational modes treated thermally. Bimolecular and unimolecular reactions are included. Both single-level and dual-level calculations may be carried out. In single-level mode, optimized geometries, potential energies, gradients, and Hessians can be calculated by any of the density functionals in the NWChem package or with the MP2 ab initio method. In dual-level mode, the lower-level data is calculated by NWChem, and the higher-level data is read in from an external file.

See http://comp.chem.umn.edu/nwchemrate for more detail.