Computational Grand Challenge: GC20893

Computational Chemical Dynamics of Complex Systems

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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 will be carried out 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 will be especially concerned with processes that enhance the design of fuel cell technology. For heterogeneous, nanoparticle, and solid-state dynamics, we will develop 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 will construct potential energy surfaces for a number of photochemical reactions and employ 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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<tr>
<td><strong>Truhlar Group</strong></td>
<td>Donald G. Truhlar, Primary Investigator</td>
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<td><strong>Siepmann Group</strong></td>
<td>J. Ilja Siepmann</td>
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<td>Kelly Anderson</td>
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<td>Jake L. Rafferty</td>
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<td>Gregory K. Schenter</td>
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<td>Ming Tsai</td>
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Number of hours allocated for FY2007
1,000,000 processor wall hours

Number of hours actually used for FY2007
924,989 processor wall hours

Request for FY2008
1,000,000 processor wall hours

Overview of the accomplishments and activities in FY2007

1. Density Functionals with Broad Applicability in Chemistry
Truhlar Group

Although density functional theory is widely used in the computational chemistry community, the most popular density functional, B3LYP, has some serious shortcomings: (i) it is better for main-group chemistry than for transition metals; (ii) it systematically underestimates reaction barrier heights; (iii) it is inaccurate for interactions dominated by medium-range correlation energy, such as van der Waals attraction, aromatic–aromatic stacking, and alkane isomerization energies. We have developed a variety of databases for testing and designing new density functionals, including databases for main-group thermochemistry, thermochemical kinetics, noncovalent interactions, transition metal chemistry, and spectroscopy. We used these data to design new density functionals, called M06-class (and, earlier, M05-class) functionals, for which we enforced some fundamental exact constraints such as the uniform-electron-gas limit and the absence of self-correlation energy. Our M06-class functionals depend on spin-up and spin-down electron densities (i.e., spin densities), spin density gradients, spin kinetic energy densities, and, for nonlocal functionals, Hartree-Fock exchange. We have developed four new functionals that overcome the above mentioned difficulties: (a) M06, a hybrid meta functional, is a functional with good accuracy “across-the-board” for transition metals, main group thermochemistry, medium-range correlation energy, and barrier heights. (b) M06–2X, another hybrid meta functional, is not good for transition metals but has excellent performance for main group chemistry, predicts accurate valence and Rydberg electronic excitation energies, and is an excellent functional for aromatic–aromatic stacking interactions. (c) M06–L is not as accurate as M06 for barrier heights but is the most accurate functional for transition metals and is the only local functional (no Hartree-Fock exchange) with better across-the-board average performance than B3LYP; this is very important because only local functionals are affordable for many demanding applications on very large systems. (d) M06-HF has good performance for valence, Rydberg, and charge transfer excited states with minimal sacrifice of ground-state accuracy. In this Account, we compared the performance of the M06-class functionals and one M05-class functional (M05-2X) to that of some popular functionals for diverse databases. We also discuss their performance on several difficult cases involving main-group thermochemistry, noncovalent interactions of biological importance, barrier heights, conformational energy, and the trend in bond dissociation energies of Grubbs’ ruthenium catalysts for olefin metathesis. Based on these tests, we recommend

1) the M06-2X, BMK, and M05-2X functionals for main-group thermochemistry and kinetics,

2) M06-2X, M05-2X, and M06 for systems where main-group thermochemistry, kinetics, and noncovalent interactions are all important,

3) M06-L and M06 for transition metal thermochemistry,

4) M06 for problems involving multireference rearrangements or reactions where both organic and transition-metal bonds are formed or broken,

5) M06-2X, M05-2X, M06-HF, M06, and M06-L for the study of noncovalent interactions,
6) M06-HF when the use of full Hartree-Fock exchange is important, for example to avoid the error of self-interaction at long-range,

7) M06-L when a local functional is required, because a local functional has much lower cost for large systems.

The availability of functionals developed in our group is described on our website:
http://comp.chem.umn.edu/info/DFT.htm.

2. Insight into the Role of Mg$^{2+}$ in Hammerhead Ribozyme Catalysis from X-ray Crystallography and Molecular Dynamics Simulation

York Group

The hammerhead ribozyme is an archetypal system to study RNA catalysis. A detailed understanding of the hammerhead mechanism provides insight into the inner workings of more complex cellular catalytic RNA machinery such as the ribosome, and ultimately may aid the rational design of new medical therapies and biotechnology.

Despite a tremendous amount of experimental and theoretical effort, the details of the hammerhead ribozyme mechanism have been elusive. In particular, one of the main puzzles involves the apparent inconsistency between the interpretation of thio effect experiments and mutational data with available crystallographic structural information of the minimal hammerhead sequence. Results from the biochemical experiments suggest that a pH-dependent conformational change, inconsistent with crystallographic data, must precede or be concomitant with the catalytic chemical step. This includes a possible metal ion bridge between the A9 and scissile phosphates that in previous crystal structures were ~20 Å apart. Moreover, the function of the 2'OH group of G8 remains unclear.

Recently, the research group of Professor Darrin York of the Department of Chemistry, U of MN, in collaboration with Professor Bill Scott of the Department of Chemistry, UCSC, have performed molecular simulations that probe the conformational and chemical events that leads to ribozyme catalysis. A series of 12 ns molecular dynamics (MD) simulations of the reactant state (with and without a Mg(II) ion), early and late transition states are presented based on a recent crystal structure of a full-length hammerhead RNA reported by Martick and Scott (Fig 1) using new molecular mechanical force field models and combined quantum mechanical/molecular mechanical potentials.

Figure 1. The full length hammerhead ribozyme.

Their simulation results support a catalytically active conformation with a Mg(II) ion bridging the A9 and scissile phosphates, preliminary data generated prior to the PNNL allocation for which has been published in a letter in *J. Chem. Theory Comput.* 3, 325-327, (2007). With the PNNL resources, these simulations are now being carried out to longer, more meaningful time scales and with a more realistic QM/MM models.

In the reactant state, the Mg(II) spends significant time closely associated with the 2'OH of G8, but remains fairly distant from the leaving group O5' position. In the early TS mimic simulation, where the nucleophilic O2' and leaving group O5' are equidistant from the phosphorus, the Mg(II) ion remains tightly coordinated to the 2'OH of G8, but is positioned closer to the O5' leaving group, stabilizing the accumulating charge. In the late TS mimic simulation, the coordination around the bridging Mg(II) ion undergoes a transition whereby the coordination with the 2'OH of...
G8 is replace by the leaving group O5’ that has developed significant charge. At the same time, the 2’OH of G8 forms a hydrogen bond with the leaving group O5’ and is positioned to act as a general acid catalyst. This work represents the first simulations of the full-length hammerhead structure and TS mimics, and provides direct evidence for the possible role of a bridging Mg(II) ion in catalysis that is consistent with both crystallographic and biochemical data. The different relative positions of the Mg(II) to key oxygen atoms are shown in Fig 2.

Further studying of the full-length hammerhead ribozyme system requires much longer simulation time hence more advanced hardware and software advances. The simulation package CHARMM has been ported to PNNL’s MPP2 supercomputer and it produces simulations of 1-1.5 ps per CPU-hour on single CPU. The maximum speedup for CHARMM running on MPP2 is 20 using 32 CPU’s thus the maximum possible speed of simulation is 500ps per day. Another simulation package, NAMD, already installed on MPP2, produces 2-3 ps per CPU-hour on a single CPU, and its maximum speedup is ~10 using 32 CPUs. Hence the maximum possible simulation speed for this Hammerhead ribozyme is ~500 ps per day on MPP2.

Much effort has been devoted to optimizing the performance of NAMD so that calculations could be run efficiently on large-scale parallel machines. The original version of NAMD at PNNL exhibited very poor scaling with the number of processors. Various compilation and inter-node network options have been tested and benchmarked. For single CPU, the performance has been improved by over 100%. For the parallel performance, the maximum speedup has been improved by a large amount. The maximum possible simulation speed for this ribozyme system now reaches ~12,000 ps per day on MPP2 due to the optimization effort. The performance improvement is illustrated in Fig 3.

Figure 2. The Radial distribution of the Mg(II)-O pairs for the proposed catalytically active Mg(II).

Figure 3. The simulation performance of the original NAMD code (PNNL old) and the optimized PNNL code (PNNL). The y-axis is the simulation time that can be obtained in one day. The x-axis is the number of CPU’s used to perform the simulation.

Our optimization effort has made much longer simulation on the hammerhead ribozyme possible on PNNL’s MPP2 system. This allows us to examine the
role of large-scale conformational events, including relaxation of the solvent and ion atmosphere, on ribozyme catalysis. The methods developed here can be broadly applied to other systems that involve biocatalysis.

3. **QM/MM Study of the H/D Kinetic Isotope Effect in the Reduction Reaction Catalyzed by Dihydrofolate Reductase (DHFR)**

   Gao and Truhlar groups

   Dihydrofolate reductase (DHFR) is a small, monomeric protein that has been extensively studied experimentally and computationally. DHFR catalyzes the reduction of 7,8-dihydrofolate (DHF) to 5,6,7,8-tetrahydrofolate (THF) with the key chemical step being the transfer of a hydride ion from the nicotinamide ring of the cofactor nicotinamide adenine dinucleotide phosphate (NADPH). At pH = 7, product release is partly rate-limiting and the H/D kinetic isotope effect is about 1.1-1.3, but the intrinsic KIE on the hydride transfer step is >3. Previously, we have investigated the catalytic mechanism and the factors that affect the reaction rate (Garcia-Viloca, M.; Truhlar, D. G.; Gao, J. "Reaction-path energetics and kinetics of the hydride transfer reaction catalyzed by dihydrofolate reductase" *Biochemistry*, 2003, **42**, 13558-13575) and have computed the temperature dependence of the kinetic isotope effects for the hydride transfer reaction.(Pu, J.; Ma, S.; Gao, J.; Truhlar, D. G. “Small Temperature Dependence of the Kinetic Isotope Effect for the Hydride Transfer Reaction Catalyzed by Escherichia coli Dihydrofolate Reductase.”( *Journal of Physical Chemistry B*, 2005, **109**, 8551-8556).

   Recently, Kohen and coworkers (PNAS, 2006, 103, 15753) described a study of the wild-type, single mutant (G121V) and double mutant (DM) (G121V and M42W) of the Escherichia coli DHFR (αDHFR) enzyme at different temperatures and reported KIE and kinetic data. Analysis of Arrehnius plots revealed the follow kinetic data: WT: $E_a = 5.6$ kcal/mol, $\Delta S = -11.8$ kcal/mol; G121V: $E_a = 5.3$ kcal/mol, $\Delta S = -12.2$ kcal/mol, and G121V/M42W: $E_a = 3.9$ kcal/mol, $T\Delta S = -15.7$ kcal/mol. This work raises interesting questions, especially concerning the contributions of enzyme dynamics to enzyme catalysis. The availability of Arrhenius parameters both for the wild-type and mutant enzymes provided an opportunity to address these questions by computation. The work has been carried out for ecDHFR at three different temperatures both for the WT and DM, by computing the potentials of mean force (PMF) and analysis of structural and kinetic parameters. The work involves multiple dynamics simulations consisting of at least 15 free energy calculations for each PMF, each lasting 200 to 500 ps. The following figures and tables summarize the results obtained so far. Additional work is being carried out to obtain a correlation of the entropic changes and structural/dynamic variations in different systems, and to obtain the corresponding KIEs.

**Fig. 1. PMF for the WT (upper) and DM(lower ) ecDHFR at different temperatures.**

![PMF Graph](null)
Figure 2 shows the corresponding Eyring plots:

Table 1 lists the computed and (in parenthesis) experimental kinetic parameters (from Eyring plots or directly from PMF simulations).

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<thead>
<tr>
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<th>Wild type</th>
<th>Double mutant</th>
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<tr>
<td>$\Delta H^\ddagger$ (kcal/mol)</td>
<td>6.35 (5.0±0.6)</td>
<td>2.06 (3.3±0.2)</td>
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<tr>
<td>$\Delta S^\ddagger$ (cal·mol⁻¹·K⁻¹)</td>
<td>-32.3 (-39.6±1.9)</td>
<td>-53.6 (-52.8±1.3)</td>
</tr>
<tr>
<td>$\Delta G^\ddagger$ at 298K (cal·mol⁻¹)</td>
<td>15.8 (16.7±0.8)</td>
<td>18.0 (19.0±0.4)</td>
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4. Thermochemical Kinetics of Hydrogen-Atom Transfers Between Methyl, Methane, Ethynyl, Ethyne, and Hydrogen
Truhlar Group

Saddle point properties of three symmetric and one asymmetric hydrogen-transfer reaction and the energies of reaction of the asymmetric reactions are investigated in the present work. These reactions,

$$H + H_2 \rightarrow H_2 + H$$  \hspace{1cm} (R1)

were calculated by various density functionals, many of which were developed in recent years, by coupled cluster theory, and by multicoefficient correlation methods based on wave function theory. Instead of comparing calculated results to “semi-experimental” values, we compared them to very accurate theoretical values (e.g., to values obtained by the Weizmann-1 method). Coupled cluster theory and the multicoefficient correlation methods MC–QCISD/3 and MCQCISD–MPW are found to be very accurate for these reactions with mean unsigned errors below 0.94 kcal/mol. Diagnostics for multireference character were calculated to aid in the interpretation and help assess the reliability of the calculations. The newly developed hybrid density functional M06-2X shows very good performance for these reactions with a mean unsigned error of only 0.77 kcal/mol; The BHandHLYP, MPW1K, and BB1K density functionals, can also predict these reactions well with mean unsigned errors less than 1.42 kcal/mol.

5. Attractive Noncovalent Interactions in the Mechanism of Grubbs Second-Generation Ru Catalysts for Olefin Metathesis
Truhlar Group

Scheme 1. First step: generation of the catalyst from the precatalysts.

Grubbs’ second-generation Ru metathesis catalysts are a hundred to a thousand times more active than first-
generation Ru metathesis catalysts, and they also exhibit greater thermal and chemical stability. The difference is the substitution of one of the phosphine ligands, usually tricyclohexylphospine, PCy3, of the bisphosphine first-generation precatalyst by a N-heterocyclic carbene (NHC), usually 1,3-dimesityl-4,5-dihydro-2-ylidene, henceforth denoted H2IMes. Liquid-phase mechanistic studies established that olefin metathesis with these 16-electron (five-coordinate) Ru precatalysts proceeds by phosphine dissociation to generate the 14-electron (four-coordinate) active species. A surprising discovery (later confirmed in the gas phase) was that phosphine dissociation in (PCy3)2Cl2Ru=CHPh (1) is faster than in (H2IMes)(PCy3)Cl2Ru=CHPh (2), so that the rate of generation of active species does not correlate with catalytic activity. Since the reverse association reaction is believed to be barrierless, the relative dissociation rates are attributed to a smaller Ru-P bond dissociation energy (BDE) in 1 than in 2 (Scheme 1). Understanding the factors that control catalyst initiation is critical to rational ligand-design strategies for new catalysts.

**Table 1.** Bond dissociation energies (kcal/mol) for the Grubbs catalysts

<table>
<thead>
<tr>
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<th>BDE(1)</th>
<th>BDE(2)</th>
<th>ΔBDE</th>
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<tr>
<td>Exp.</td>
<td>-3.4 ± 2 (a)</td>
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<tr>
<td>M06-L/TZQ</td>
<td>36.1</td>
<td>40.2</td>
<td>-4.1</td>
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<td>M06-L/TZQ-CP (b)</td>
<td>34.2</td>
<td>38.2</td>
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<td>M06-L/DZQ</td>
<td>41.7</td>
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<td>M06-L/DZQ-CP</td>
<td>38.3</td>
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<td>B3LYP/DZQ</td>
<td>19.0</td>
<td>17.4</td>
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<tr>
<td>B3LYP/DZQ-CP</td>
<td>15.6</td>
<td>14.0</td>
<td>1.7</td>
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<td>BP86/DZQ</td>
<td>20.0</td>
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<td>26.1</td>
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<td>PBEh/DZQ</td>
<td>28.9</td>
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<td>TPSSh/DZQ</td>
<td>24.6</td>
<td>23.5</td>
<td>1.1</td>
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Remove RuCl2 \(c\)

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<tr>
<th>Method</th>
<th>BDE(1)</th>
<th>BDE(2)</th>
<th>ΔBDE</th>
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<tr>
<td>M06-L/DZQ</td>
<td>9.9</td>
<td>14.4</td>
<td>-4.5</td>
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<tr>
<td>B3LYP/DZQ</td>
<td>-4.5</td>
<td>-8.0</td>
<td>3.5</td>
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\(a\)As inferred from experiment. \(b\)Results marked CP are corrected for the basis set superposition error by the counterpoise approach. \(c\)We removed the Ru\(^{2+}\) cation and the two Cl\(^-\) anions from the complexes, without reoptimizing the geometries of either the original complexes or their dissociation products.
1 and 2, with a difference of -4.5 kcal/mol. This explains the sign of the ΔBDE value of the original complexes. The positive BDEs, even in the absence of Ru, shows that the noncovalent interactions between the large ligands are attractive. However, the B3LYP functional give a negative BDE and the sign of ΔBDE for demetalized 1 and 2. This is consistent with results for test suites on which we have found that M06-L is more accurate than the other functionals considered above for both noncovalent interaction energies and metal-ligand bond energies.

We conclude that noncovalent attractive interactions between the large ligands in the precatalysts play a decisive role in the effect of ligand variation on the mechanism and activity of ruthenium-based olefin metathesis. The roles of covalent and dative electronic effects (electron-donating effects) and noncovalent repulsive interactions (steric effects) have been widely discussed, but the noncovalent attractive interactions have been ignored in previous work. The ability of new density functionals to analyze and accurately model such attractive interactions due to medium-range correlation energy opens new possibilities for computer-aided catalyst design.

6. **Size-Selective Supramolecular Chemistry in a Hydrocarbon Nanoring**
   Truhlar Group

New-generation density functionals (M06-L and M06-2X) include an accurate treatment of medium-range correlation energy and have been applied to investigate host-guest interactions in supramolecular complexes in which a carbon nanoring, [6]paraphenyleneacetlene ([6]CPPA), acts as the host molecule. Guests include fullerenes and carbon nanotubes. The nature of the interactions has been discussed and analyzed. The size-selective supramolecular chemistry in the nanoring has been investigated by varying the size of the guest molecules and optimizing inclusion structures as large as C_{128}H_{44}. We found that the (5,5) armchair-type nanotube fits in the [6]CPPA hydrocarbon nanoring better than the (3,3) or (4,4) ones, and C70 is bound more strongly than C60. The predicted host-guest binding energies of the (4,4), (5,5), C60, and C70 structures are 24, 43, 25, and 28 kcal/mol, respectively.

7. **Free Energies of Formation of Metal Clusters and Nanoparticles from Molecular Simulations**
   Truhlar and Siepmann Groups

Metal nanoparticles are important in several emerging technologies, but their size-selected thermodynamic properties are hard to obtain from experiment. We have calculated the global and local
minima of unsupported neutral Al\(_n\) (2 \(\leq n \leq 65\)) particles (clusters and nanoparticles) by combining big-bang random searches with molecular dynamics quenching and using a recently validated many-body analytic potential. The distribution of the local energy minima and the finite-temperature thermodynamics of the Al\(_n\) particles have been calculated, the latter by evaluating the rovibrational partition functions of the low-energy isomers. This analysis indicates that structural stability depends on temperature, and that one must consider statistical mechanics as well as electronic structure in determining the properties of nanoparticles. Some particles with electronic magic numbers are shown to become unstable at elevated temperatures, when one considers thermal and entropy effects. The electronic magic numbers are \(n = 13, 19, 23, 38,\) and 55, but \(n = 28\) becomes unstable at elevated temperatures. Furthermore, for several \(n\), the global minimum of potential energy need not be the dominant structure at moderate temperatures, and the second- or third-lowest-energy isomer may be dominant at temperatures as low as room temperature. The isomeric energy \((E_{\text{Iso}})\), which is the difference between the thermal average energy of the particle in the ground electronic state and thermal average energy of the structure corresponding to the global minimum in the ground electronic state, is an indicator of how well the thermochemical properties of a multi-isomer particle can be represented by those of the global minimum, and we calculate \(E_{\text{Iso}}\) for \(n = 2–65\).

We also characterize the energy landscapes by determining the probability of finding the second, third, and fourth lowest-energy structures as a function of particle size, temperature and isomer energy.

An efficient simulation method was developed for determining the standard Gibbs free energy changes for the reactions, \(M + M_{n-1} \leftrightarrow M_n\) (R1), involved in the formation of atomic clusters and nanoparticles (also called particles) in the vapor phase. The standard Gibbs free energy of formation \((\Delta_f G^\circ)\) of particles is obtained from these Gibbs free energy changes \((\Delta G^\circ)\) by a recursion relationship using the experimental \(\Delta_f G^\circ\) of the monomer. This method has been applied to reactions involving Al\(_n\) particles with \(n = 2 – 60\). This method has been validated for \(n = 2\), where the experimental thermodynamic properties of Al\(_2\) have been recompiled using the latest available experimental or accurate theoretical data. For \(n = 2–4\), two completely different approaches, a Monte Carlo configuration integral (MCCI) integration of partition functions and an aggregation-volume-bias Monte Carlo (AVBMC) direct simulation of the equilibrium constants, employing four well validated potential energy functions have been used to calculate \(\Delta G^\circ\) of R1. Excellent agreement is observed for these two methods. Although different potential energy functions give different stage-1 results for \(n \leq 10\), three high-level correction (HLC) terms, namely a correction for the potential energy difference of the global minima, another for the electronic excitation contribution, and a third based on calculating isomeric-rovibrational contributions have been applied to mitigate deficiencies in the potential energy functions. For \(n = 2\), good agreement has been found between the corrected simulation results and experimental data. For larger \(n\), the more efficient AVBMC method has been used. Finally, accurate \(\Delta G^\circ\) of R1 and thus \(\Delta_f G^\circ\) of Al\(_n\) particles with \(n = 2 – 60\) have been determined. This is the first example of the determination of nanoparticle free energies of formation.

The association reactions of Al atom with Al\(_n\) particles, and the unimolecular dissociation of Al\(_n\) particles have been studied using classical molecular dynamics trajectory simulations. Thermal reaction rate constants of both reactions have been determined; these rate constants are the key parameters of clustering mechanisms for particle growth. It was found that the
association rate constants depend weakly on
temperature, and the reaction is barrierless. For the
unimolecular dissociation reactions, the rate constant
depends strongly on temperature and is fitted using the
Arrhenius equation. The results indicate that the
unimolecular dissociation reaction has a high activation
barrier that tends to increase with particle size. The
results indicate that monomer emission is always the
dissociation process with the largest rate constant. With
both the forward (monomer association) and backward
(monomer emission) rate constants, the standard Gibbs
free energy changes of the $\text{Al} + \text{Al}_{n-1} \leftrightarrow \text{Al}_n$ reactions
with $n = 2 – 60$ have been determined. The standard
Gibbs free energy changes determined by the molecular
dynamics simulations agree fairly well with those
determined by our previous Monte Carlo equilibrium
simulations.

8. Hybrid Approach for Excited States and for Free
Energy Calculations with High-Level Methods

PNNL

Evolution of the excited state energies of cytosine
base in the native DNA environment was investigated
using a hybrid coupled cluster and classical molecular
dynamics approach. The time averaged excitation
energies obtained with the variant of the completely
renormalized equation-of-motion with singles, doubles,
and non-iterative triples approach that includes a bulk of
the correlation effects for excited states, are compared
with the analogous calculations in the gas phase.
Significant blue shifts for the two lowest singlet
excitation energies can be observed as a result of the
interaction of the quantum system with the surrounding
environment.

We also present an approach to calculate the free
energy profile along a condensed-phase reaction path
based on high-level electronic structure methods for the
reactive region. The bulk of statistical averaging is
shifted toward less expensive descriptions by using a
hierarchy of representations that includes molecular
mechanics, density functional theory, and coupled
cluster theories. As an application of this approach we
study the reaction of CHCl$_3$ with OH$^-$ in aqueous
solution.

Proposed research in FY2008

1. Developments and Applications of DFT

We plan to implement the M06-class functionals in
plane-wave code for solids simulations. We plan to
complete calculations on two buckyball tweezers, and we
will study torsional potentials for several conjugated
systems.

2. Zeolite Catalysis

We will develop a benchmark database of
interaction energies in zeolite model complexes, and we
will also employ this database to validate many electronic
structure methods. We will apply the M06-class
functionals for heterogeneous catalysis simulations in
zeolite.

3. Development of Solvation Models

During the on-going period we have finalized the
new universal continuum solvation model (where
“universal” denotes applicable to all solvents), called
SM8. This model is based on the generalized Born
approximation. The SM8 model improves on earlier
universal solvation models developed at the University
of Minnesota, and it substantially outperforms the
default solvation methods implemented in popular
computational programs.

The next step is an extension of SM8 to the Poisson
equation formalism as an alternative to the generalized
Born equation for computation of the electrostatics.
The parametrization of SM8 based on the Poisson-
Boltzmann solver implemented in Jaguar and based on
PCM/GAMESS is in progress now and it will be
continued during the next allocation period.
4. **Computational Electrochemistry**

We will continue our work on computational electrochemistry. Although the recent SM8 model has been developed using a rather large training set of neutral solutes and singly-charged ions in water and various organic solvents, it seems to be interesting to study the applicability of the new model toward predicting the properties of different classes of compounds, for instance, transition metal ions in aqueous solution. This project is broadly defined. The properties of interest are liquid-phase molecular geometries of transition metal complexes, stationary points on the potential energy surfaces of solvated species, complex stability constants, hydrolysis constants, or/and standard redox potentials.

We have also been working on the development of a new consistent set of van der Waal’s radii.

5. **Dynamics of Phospholamban and the Ammonia Transport Mechanism through a Channel Protein**

We will investigate the structure and dynamics of phospholamban, a pentameric transmembrane protein that regulates the Ca-ATPase, and the ammonia transport mechanism through a channel protein.

6. **Electrostatically Embedded Many-Body Method**

During past terms we also developed the electrostatically embedded many-body (EE-MB) method for calculating the energetics of large molecular clusters. The EE-MB method carries out a many-body expansion of the total energy and embeds each fragment in a field of point charges to represent the other molecules in the cluster. We have extended the EE-MB method to computation of correlation energy only (EE-MB-CE). This new method carries out an electrostatically embedded many-body expansion of the correlation energy, combined with a Hartree-Fock calculation of the entire cluster. We plan to extend this method to periodic systems, to use it for the optimization of large water clusters, to examine the choice in charge model for other types of molecular clusters, such as water-ammonia clusters, and to extend it to treat biopolymers.

7. **Hybrid Ab-initio Methods for Free Energy Calculations**

We will continue our work on the development of free energy methods utilizing hybrid ab-initio and molecular mechanics descriptions. We will extend our optimizations, reaction pathway and free energy methods to coupled cluster quantum mechanical description of the reactive regions. This will position us to address a wide range problems pertaining not only to ground but also excited states. The potential application in this part of the project will include reaction rates, electron transfer processes, adiabatic excitations and ionization potentials in both aqueous and heterogeneous environments such biopolymers.

**List of publications, 2006-2007**


"Density Functionals with Broad Applicability in..."

List of presentations


“New density functionals for making bold predictions,” Y. Zhao and D. G. Truhlar, 234th ACS National Meeting, Boston, MA, 2007

“Development and use of a small representative benchmark suite for thermochemical kinetics.,”


List of significant methods, routines or codes

MN-NWChemFM
http://comp.chem.umn.edu/mn-nwchemfm/

MN-NWChemFM (Minnesota NWChem Functional Module) is a module written in FORTRAN 90 for incorporation of the M06 suite of density functionals into NWChem-version 5.0. MN-NWChemFM adds the following new capabilities to NWChem-version 5.0:

- The M06-L, M06-HF, M06, and M06-2X Density Functionals
- VS98 (also called VSXC) Functional

MN-NWChemFM has been employed in the following papers:
