Contract Information

Contract Number	N00014-05-1-0538
Title of Research	Integrated Tools for Computational Chemical Dynamics
Principal Investigator	Donald G. Truhlar
Organization	UNIVERSITY OF MINNESOTA

Technical Section

Technical Objectives

The goal of this project is to develop powerful simulation methods and incorporate them into a user-friendly high-throughput integrated software suite for chemical dynamics.

Technical Approach

We are 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:

- thermochemical kinetics and rate constants, including catalysis
- photochemistry and spectroscopy
- chemical and phase equilibria
- solvation and electrochemistry

Progress Statement Summary

We are focusing on addressing the challenges of accurately treating both the energetics and dynamics of molecular processes in condensed phases. The project consists of the three sections (computational electrochemistry, heterogeneous catalysis, and computational photochemistry), each of which involves software for a particular area of condensed-phase chemistry, and our goal is to further develop this software and better integrate it. This includes tools for calculating reaction rates and transport properties and for investigating energetic processes, catalysis, and dynamics. In the computational electrochemistry area, we have developed and improved models for general electrochemical processes, with special attention to tools that can enhance the design of fuel cell technology. We have developed protocols for calculating relevant thermodynamic and kinetic parameters (for instance, redox potentials) and computational software for carrying out calculations based on these protocols. For heterogeneous catalysis, we have developed an array of methods for multi-time-scale simulation. Other projects include the development of new adaptive schemes and many-body tight-binding theory. The algorithms being developed are general enough to apply to a variety of problems, for example, catalysis in zeolites, catalysis on surfaces of metals and metal oxides, catalysis by and on nanoparticles, and partitioning and reactivity of aqueous solutions containing electrolytes at metal/water interfaces. In the computational photochemistry area, we have developed methods and software for excited state energies in the gas phase and we are working on those for the solution phase, as required to address condensed-phase effects on the excitation energies and couplings, couplings between excited states in the gas phase and the liquid phase, and new dynamics methods for non-Born-Oppenheimer processes in gaseous and liquid phases.

Progress, Aug 2007 – July 2008

This section contains several subproject reports on the work we have carried out in the 2007/2008 financial year for the Integrated Tools for Computational Chemical Dynamics project.

Subproject no. 1:
Density Functional Theory: Development and Integration

Yan Zhao and Donald G. Truhlar

We have finalized the implementation of our recently developed M06 suite of density functionals (namely, M06-L, M06, M06-HF, and M06-2X where 'M' stands for Minnesota) into several popular computational programs:
- The Amsterdam Density Functional (ADF) package (Version ADF2007)
- *GAMESS* (Version R1, April 11, 2008)
- *Jaguar* (Version 7.0.207)
- *NWChem* (Version 5.1)
- *Q-Chem* (Version 3.1)

Our work on the integration of the density functionals into the above-mentioned computational packages includes the transfer of model parameters to the developers of the software or/and the transfer of computational codes. We are also involved in testing the final versions of the computational packages incorporating our models.

The Minnesota density functionals such as M06 outperform many other functionals (for instance, the most popular functional, B3LYP) on several difficult cases involving problems with main-group thermochemistry, noncovalent interactions, weakly bound complexes, multireference rearrangements, barrier heights, conformational energy, and those reactions where both organic and transition-metal bonds are formed or broken.

The M06 suite of functionals all depend on kinetic energy density; hence they are meta GGAs (M06-2L) and hybrid meta GGAs (M06, M06-2X, ans M06-HF). We have also developed a specialized density functional method on the generalized gradient approximation (GGA) without meta or hybrid components. The new generalized gradient approximation has no empirical parameters. The new GGA is exact through second order, and it is called the second-order generalized gradient approximation (SOGGA). It yields very accurate lattice constants of solids.

Subproject no. 2:
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 self-assembly 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 $\pi...\pi$ 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.

$C_{60}@C_{60}H_{28}$
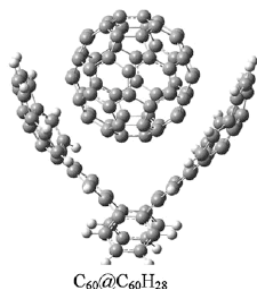
One of the most exciting topics of the project is an application of the Minnesota density functionals (M06-L and M06-2X) to study the geometries and binding energies of a recently synthesized tweezers-like buckyball catcher ($C_{60}H_{28}$) and its supramolecular complexes with buckminsterfullerene C_{60} (see the figure). The $C_{60}H_{28}$ buckycatcher has two corannulene pincers and a tetrabenzo-cyclo-octatetraene 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.

Subproject no. 3:
Modeling of Solvation Effects

Aleksandr V. Marenich, Ryan M. Olson, Adam C. Chamberlin, 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 in terms of the Integral-Equation-Formalism Polarizable Continuum Model (IEFPCM) 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 IEFPCM model and the Conductor-like Polarizable Continuum Model (CPCM) implemented in *Gaussian 03* and *GAMESS*, and it can be used in conjunction with the Generalized Conductor-like Screening Model (GCOSMO) implemented in *NWChem*.

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).

Default   **SMD**
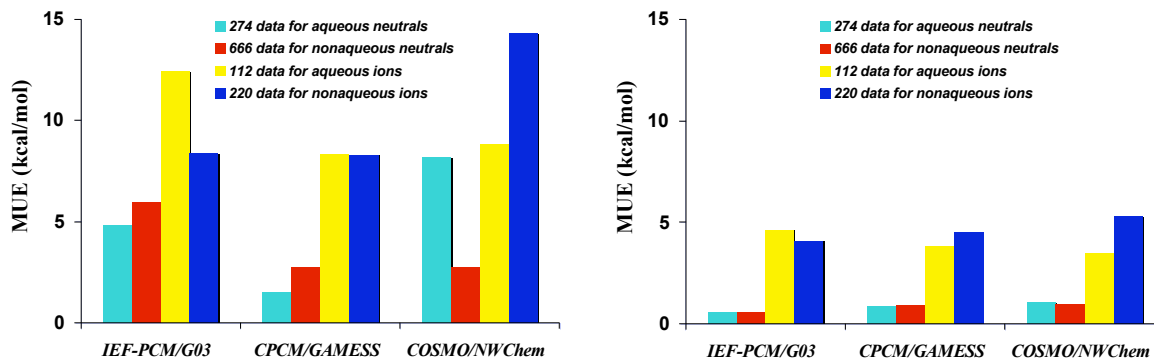
The new SMD model will complement the recent SM8 model based on the generalized Born equation for electrostatics. In addition, an improved version of SM8 with improved electrostatics (SM8IE) will be developed.

We have extended our temperature-dependent solvation model (SM6T) to predict free energies of solvation as a function of temperature for a variety of solutes in aqueous solution. The updated SM6T, now denoted SM8T, can account for the temperature dependence of the free energy of solvation for H, C, N, O, F, S, Cl, and Br-containing neutral compounds in water.

We have also finalized a solvation model for olive oil as a solvent.

We have begun the incorporation of our solvation models developed under the project 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. The software developed under the grant is being tested extensively to validate its compatibility, portability, and bug-free status on various computer platforms including but not limited the following specifications:

Machine/Processor	Operating System	Compiler
Regatta IBM Power 4	AIX version 5.2	XL Fortran version 9.1
SGI Altix Intel Itanium 2	SUSE Linux 2.6.5	Intel version 8.1-10.1, gfortran gcc 4.2.4
IBM Blade Center AMD Opteron	SUSE Linux 2.6.5	Intel version 8.1, PGI version 6.2
SGI Altix XE 1300 Intel Xeon	SUSE Linux 2.6.16	Intel version 10.1, gfortran gcc 4.1.2

The earlier SM8 model has been incorporated into the *GAMESSPLUS* computational program that is designed to work with the latest revision of *GAMESS* (11 April, 2008). Since the latest revision of *GAMESS* includes the Minnesota suite of density functionals (namely, M06-L, M06, M06-HF, and M06-2X) the integrated *GAMESSPLUS* implementation of SM8 allows for exploration of a promising combination of the newest and most accurate (up-to-date) solvation models with the highly effective density functionals. The current version of *GAMESSPLUS* is also compatible with an older revision of *GAMESS* (the *GAMESS* version of March 24, 2007).

The SMD model has been incorporated into the Gaussian External Solvation module (*GESOL*) that is designed to work with *Gaussian 03* (revision D.01 and later). Thus the users of *Gaussian 03* can benefit from the extended functionality of this popular program.

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Subproject no. 4:
Design of a Next Generation Force Field

Wangshen Xie, Luke Fiedler, Jiali Gao, and Donald G. Truhlar

An electronic structure-based polarization method, called the X-POL potential, has been described for the purpose of constructing an empirical force field for modeling polypeptides. The X-POL potential is a quantum mechanical model, in which the internal, bonded interactions are fully represented by an electronic structure theory augmented with some empirical torsional terms. Nonbonded interactions are modeled by an iterative, combined quantum mechanical and molecular mechanical method, in which the molecular mechanical partial charges are derived from the molecular wave functions of the individual fragments. The feasibility of such and electronic structure based force field is illustrated by small model compounds. A method has been developed for separating a polypeptide chain into peptide units, and its parametrization procedure in the X-POL potential is documented and tested on glycine dipeptide. We envision that the next generation of force fields for biomolecular polymer simulations will be developed based on electronic structure theory, which can adequately define and treat many-body polarization and charge delocalization effects. Continuing work involves the reparametrization of AM1 to yield improved polarizabilities.

Subproject no. 5:
Quantum Mechanical/Molecular Mechanical Simulation Methods For Catalysis

Kwangho Nam, Jiali Gao, and Darrin M. York

The molecular mechanism of hairpin ribozyme catalysis is studied with molecular dynamics simulations using a combined quantum mechanical and molecular mechanical (QM/MM) potential with a recently developed semiempirical AM1/d-PhoT model for phosphoryl transfer reactions. Simulations are used to derive one- and two-dimensional potentials of mean force to examine specific reaction paths and assess the feasibility of proposed general acid and base mechanisms. Density-functional calculations of truncated active site models provide complementary insight to the simulation results. The computational methods are general and may also be used for heterogeneous catalysis.

Subproject no. 6:
Zeolite Catalysis

Bo Wang, Andreas Heyden, Jake Rafferty, J. Ilja Siepmann, and Donald G. Truhlar

We are developing 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.