

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 addressing the challenges of accurately treating both the energetics and dynamics of molecular processes in condensed phases. We are doing this by integrating state-of-the-art software that may be used for simulations, focusing on addressing the challenges of accurately treating both the energetics and dynamics of molecular processes in condensed phases. In particular, we are developing and improving models for general electrochemical processes, for calculating relevant thermodynamic and kinetic parameters. In 2008-2009, we developed and validated a new Grand Canonical Monte Carlo program for the simulation of adsorption isotherms involved in heterogeneous catalysis. We also created a computer package for the treatment of the explicit polarization of macromolecular systems based on the X-Pol method which was designed as a next-generation force field for modeling the dynamics and reactivity of systems of chemical and biological interest in condensed phases. We have been developing protocols for calculating relevant thermodynamic and kinetic parameters (for instance, redox potentials and equilibrium constants) and computational software for carrying out calculations based on these protocols. During the past year two of our solvation models were incorporated in JAGUAR (Schrödinger, Inc.) and in GAUSSIAN 09 (Gaussian, Inc).

Progress, Aug 2008 – July 2009

This section contains several subproject reports on the work we have carried out in the 2008/2009 financial year for the Integrated Tools for Computational Chemical Dynamics project.

Subproject no. 1: Modeling of Solvation Effects

Aleksandr V. Marenich, Christopher J. Cramer, and Donald G. Truhlar

We have developed a new self-consistent reaction field continuum solvation model based on the generalized Born (GB) approximation for the bulk electrostatic contribution to the free energy of solvation. The new model improves on the earlier SM8 model by using the asymmetric descreening algorithm to treat dielectric descreening effects rather than the Coulomb field approximation. The new model is called Solvation Model 8 with asymmetric descreening (SM8AD). The SM8AD model is applicable to any charged or uncharged solute in any solvent or liquid medium for which a few key descriptors are known, in particular dielectric constant, refractive index, bulk surface tension, and acidity and basicity parameters. It does not require the user to assign molecular mechanics types to an atom or a group; all parameters are unique and continuous functions of geometry. This model employs a single set of parameters (solvent acidity-dependent intrinsic Coulomb radii for the treatment of bulk electrostatics and solvent description-dependent atomic surface tensions coefficients for the treatment of nonelectrostatic and short-range electrostatic effects). The SM8AD model was optimized over 26 combinations of theoretical levels including various basis sets (MIDI!, 6-31G*, 6-31+G*, 6-31+G**, 6-31G**, cc-pVDZ, DZVP, 6-31B*) and electronic structure methods (M05-2X, M05, M06-2X, M06, M06-HF, M06-L, mPW1PW, mPWPW, B3LYP, HF). It may be used with confidence with any level of electronic structure theory as long as self-consistently polarized Charge Model 4 or other self-consistently polarized charges compatible with CM4 charges are used, for example, CM4M charges can be used. With M05-2X/6-31G*, the SM8AD model achieves a mean unsigned error of 0.6 kcal/mol on average over 2560 solvation free energies of tested aqueous and nonaqueous neutral solutes and a mean unsigned error of 3.9 kcal/mol on average over 332 solvation free energies of aqueous and nonaqueous ions.

We continue 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.

Subproject no. 2: Improvements in the Feynman Path Integral Methods

Steven L. Mielke and Donald G. Truhlar

We have made two enhancements to our methods previously developed for calculating vibrational–rotational free energies by Feynman path integrals, namely, a sequential sectioning scheme for efficiently generating random free-particle paths and a stratified sampling scheme that uses the energy of the path centroids. These improved methods were used with three interaction potentials to calculate equilibrium constants for the fractionation behavior of Cl⁻ hydration in the presence of a gas-phase mixture of H₂O, D₂O, and HDO. Results of a variety of electronic structure calculations, including coupled cluster and multireference configuration interaction calculations, with either the harmonic oscillator – rigid rotor approximation or with anharmonicity estimated via second-order vibrational perturbation theory, all agree well with the equilibrium constants obtained from the analytical surfaces.

Subproject no. 3:
Construction of Diabatic and Adiabatic Potential Energy Surfaces Based on Ab Initio Valence Bond Theory

Lingchun Song and Jiali Gao

We have developed a theoretical model for deriving effective diabatic states based on ab initio valence bond self-consistent field (VBSCF) theory by reducing the multiconfigurational VB Hamiltonian into an effective two-state model. We describe two computational approaches for the optimization of the effective diabatic configurations, resulting in two ways of interpreting such effective diabatic states. In the variational diabatic configuration (VDC) method, the energies of the diabatic states are variationally minimized. In the consistent diabatic configuration (CDC) method, both the configuration coefficients and orbital coefficients are simultaneously optimized to minimize the adiabatic ground-state energy in VBSCF calculations. In addition, we describe a mixed molecular orbital and valence bond (MOVB) approach to construct the CDC diabatic and adiabatic states for a chemical reaction. Note that the VDC-MOVB method has been described previously. Employing the symmetric S_N2 reaction between NH_3 and $CH_3NH_3^+$ as a test system, we found that the results from ab initio VBSCF and from ab initio MOVB calculations using the same basis set are in good agreement, suggesting that the computationally efficient MOVB method is a reasonable model for VB simulations of condensed phase reactions. The results indicate that CDC and VDC diabatic states converge, respectively, to covalent and ionic states as the molecular geometries are distorted from the minimum of the respective diabatic state along the reaction coordinate. Furthermore, the resonance energy that stabilizes the energy of crossing between the two diabatic states, resulting in the transition state of the adiabatic ground-state reaction, has a strong dependence on the overlap integral between the two diabatic states and is a function of both the exchange integral and the total diabatic ground-state energy.

Subproject no. 4:
The X-Pol Computational Package

Wangshen Xie, Jiali Gao, and Donald G. Truhlar

We have developed a computer package for the treatment of the explicit polarization of macromolecular systems based on the explicit polarization (X-Pol) approach. 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 an 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. In the past year we implemented the X-Pol method using ab initio Hartree-Fock theory and hybrid density functional theory. The computational results were illustrated by considering a set of bimolecular complexes of small organic molecules and ions with water. The computed interaction energies and hydrogen bond geometries were in good accord with CCSD(T) calculations and B3LYP/aug-cc-pVDZ optimizations.

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

Jake L. Rafferty and J. Ilja Siepmann

One of the key processes involved in heterogeneous catalysis is the adsorption/desorption of reactants and products from the active site of the catalyst. Often, this process involves complicated phenomena such as the interaction of adsorbate π -bonds with the catalyst surface. These phenomena become apparent, for example, in the differing adsorption properties of alkanes and alkenes with various zeolites. In a typical molecular mechanics force field the interaction parameters for alkanes and alkenes are usually quite similar and, therefore, simulations using these force fields may not be adequate to reproduce differences in adsorption properties. Thus, in an effort to more accurately model the complicated phenomena involved in adsorption/desorption, a quantum mechanical approach will be taken. The work undertaken here is aimed at developing novel simulation methods capable of modeling complex adsorption phenomena at multiple levels of theory. Specifically, a Grand Canonical Monte Carlo (GCMC) module for the simulation of adsorption isotherms has been written and validated. Work is still ongoing on integrating this GCMC module with more sophisticated QM/MM routines to compute configuration energies.

**Subproject no. 6:
Thermodynamics of Associating Fluids**

Kelly E. Anderson, Mohammad Dinpajoo, J. Ilja Siepmann, and Donald G. Truhlar

One of the key bottlenecks in simulations of fluid systems that can associate via the reversible or non-reversible formation of hydrogen bonds or chemical bonds, is the efficient sampling of the aggregate size and architecture distributions. That is, aggregate/cluster growth or shrinkage evolve on timescales that are orders of magnitude longer than the timescales for the relaxation of molecular translations and rotations. We have developed special types of Monte Carlo moves (aggregation-volume-bias Monte Carlo algorithm) that can overcome these sampling problem. Furthermore, we have demonstrated that the Ewald summation technique is not required for the accurate calculation of the electrostatic energy in gas phases with low to moderate density (including strongly aggregated vapors with compressibility factors much smaller than unity. These methods have been implemented into the software packages CP2K (cp2k.berlios.de) and MCCC (towhee.sourceforge.net). Both of these packages are available via a GNU general public license.