July 31, 2007

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

FACULTY INVESTIGATORS

Donald G. Truhlar, Principal Investigator
Christopher J. Cramer
Jiali Gao
J. Ilja Siepmann
Darrin York

PNNL INVESTIGATORS

Bruce Garrett, co-PI
Michel Dupuis
Shawn Kathmann
Greg Schenter
Marat Valiev

PROJECT MANAGER

Yan Zhao, Ph. D.

POSTDOCTORAL ASSOCIATES

Alek Marenich, Ph. D.
Ryan Olson, Ph. D.
Pablo Jaque, Ph. D.

GRADUATE STUDENTS

Kwangho Nam
Jake Rafferty

ABSTRACT

The goal of this project is to develop more powerful simulation methods and incorporate them into a user-friendly high-throughput integrated software suite for chemical dynamics. The integrated software suite will combine electronic structure packages with dynamics codes and efficient sampling algorithms for the following kinds of condensed-phase modeling problems:

• thermochemical kinetics and rate constants

• photochemistry and spectroscopy

• chemical and phase equilibria

The research is focused on three application areas, in particular, electrochemistry, heterogeneous catalysis, and photochemistry. The most significant achievements of this project for Aug. 2006 - July 2007 are:

• We developed the new powerful M06-class density functionals and implemented them in two software modules namely MN-GFM and MN-NWCHEMGFM. The new functionals have been shown to give excellent performance for main-group thermochemistry, thermochemical kinetics, noncovalent interactions, transition metal chemistry, and spectroscopy. The new functionals have been applied to study supramolecular assembly, olefin metathesis, nucleobase pair stacking, and graphene material.

• We have designed a new QM/MM computational methodology that allows self-consistent polarization of the boundary in the redistributed charge and dipole scheme.

• The SM8 continuum model is designed to include condensed-phase effects for both aqueous solution and organic solvents in classical and quantum mechanical electronic structure calculations and can also be used for calculating free energies, solubilities, vapor pressures, geometries, and vibrational frequencies in condensed phases. SM8 is a self-consistent reaction field model for aqueous and nonaqueous solutions based on accurate polarized partial charges**.**

• We have developed a strategy for adaptive partitioning in combined quantum mechanical and molecular mechanical calculations of potential energy functions for multiscale simulations.

• We have developed two interface program for dynamics: JAGUARATE and NWCHEMRATE.

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
- photochemistry and spectroscopy
- chemical and phase equilibria

Progress, Aug 2006–July 2007

This section contains several subproject reports on work we have carried out in the first year and a quarter for the Integrated Tools for Computational Chemical Dynamics project. The University of Minnesota personnel supported in whole or in part by this grant are underlined. Additional contributions (see publication list and technology transfer section) have been made by University of Minnesota investigators supported by other funds, for example fellowship funds or complementary grants, and their contributions represent added leverage for the Integrated Tools for Computational Chemical Dynamics project.

Subproject no. 1: Integrated Tools Software

Update of Two DFT Modules (MN-GFM and MN-NWCHEMFM)

Yan Zhao and Donald G. Truhlar

We implemented our recently developed density functionals (M06-L, M06, M06-HF, and M06-2X) into two modules: Gaussian03 (MN-GFM 3.0) and NWChem (MN-NWCHEMFM 2.0). These newly developed functionals have improved performances for main group thermochemisitry, transition metal bonding, thermochemical kinetics, and noncovalent interactions.

Subproject no. 2: Methodology and Integrated Tools Software

Self-Consistent Polarization of the Boundary in the Redistributed Charge and Dipole Scheme for Combined Quantum-Mechanical and Molecular-Mechanical Calculations

Yan Zhang, Hai Lin, and Donald G. Truhlar

The recently developed redistributed charge (RC) and redistributed charge and dipole (RCD) schemes are electrostatic-embedding schemes to treat a quantum-mechanical/molecular-mechanical (QM/MM) boundary that passes through covalent bonds. In the RC and RCD

schemes, the QM subsystem is polarized by the MM subsystem, but the MM subsystem is not polarized by the QM one; this results in an unbalanced treatment of the electrostatic interactions. In the work reported here, we developed improved schemes, namely, the polarized-boundary RC scheme (PBRC) and the polarized-boundary RCD (PBRCD) scheme, by adding self-consistent mutual polarization of the boundary region of the MM subsystem to the previous schemes. The mutual polarizations are accounted for in the polarized-boundary calculations by adjusting the boundary-region MM point charges according to the principles of electronegativity equalization and charge conservation until the charge distributions in both the QM subsystem and the polarizable region of the MM subsystem converge. In particular, we implemented three literature parametrizations of electronegativity equalization: the original electronegativity equalization method (EEM) by Mortier and co-workers, the charge equalization (QEq) method proposed by Rappe and Goddard, and a modified version of the QEq method by Bakowies and Thiel. The PBRC and PBRCD schemes were tested by calculating proton affinities for small organic compounds and capped amino acids. As compared to full-QM calculations, the PBRC and PBRCD schemes produced more accurate proton affinities, on average, than the original RC and RCD methods; the mean unsigned error in proton affinities is reduced from about 5 kcal/mol to 3 kcal/mol with little change in geometry. The improvement is encouraging and illustrates the importance of mutual polarization of the QM and MM subsystems in treating reactions where noticeable charge transfer occurs in the QM subsystem.

Subproject no. 3: Methodology and Integrated Tools Software

A Density Functional Theory that Accounts for Medium-Range Correlation Energies in Organic Chemistry

Yan Zhao and Donald G. Truhlar
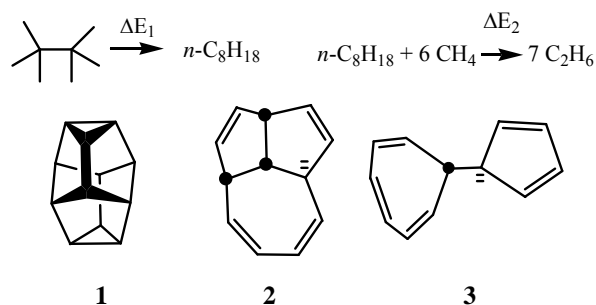
Relative energies in kcal/mol

	ΔE_1	ΔE_2	$E_2 - E_1$	$E_3 - E_1$
Best est.	1.9	19.8	14.3	25.0
B3LYP	-8.4	11.8	-0.2	1.9
M05-2X	1.4	16.8	16.9	25.4

It has recently been pointed out that current density functionals are inaccurate for computing stereoelectronic effects and energy differences of isomerization reactions and isodesmic reactions involving alkanes; this has been interpreted as an incorrect prediction of medium-range correlation energies. This letter shows that the recently published M05-2X functional has good

accuracy for all three of the recently highlighted problems and should be useful for a wide variety of problems in organic chemistry.

Subproject no. 4: Methodology and Integrated Tools Software

Density Functional for Spectroscopy: No Long-Range Self-Interaction Error, Good Performance for Rydberg and Charge-Transfer States, and Better Performance on Average than B3LYP for Ground States

Yan Zhao and Donald G. Truhlar

DFT for Long-Range Charge Transfer

We present a new density functional called M06-HF. The new functional has full Hartree-Fock exchange, and therefore it eliminates self-exchange interactions at long range. This leads to good performance in TDDFT calculations of both Rydberg and charge transfer states. In addition the functional satisfies the uniform electron gas limit, and it is better than the popular B3LYP functional, on average, for ground-electronic-state energetics.

Subproject no. 5: Electrochemistry and Integrated Tools Software

SMx Continuum Models for Condensed Phases

Christopher J. Cramer and Donald G. Truhlar

The SMx continuum models are designed to include condensed-phase effects in classical and quantum mechanical electronic structure calculations and can also be used for calculating geometries and vibrational frequencies in condensed phases. Originally developed for homogeneous liquid solutions, the SMx models have seen substantial application to more complicated condensed phases as well, e.g., the airwater interface, soil, phospholipid membranes, and vapor pressures of crystals as well as liquids. Bulk electrostatics are accounted for via a generalized Born formalism, and other physical contributions to free energies of interaction between a solute and the surrounding condensed phase are modeled by environmentally sensitive atomic surface tensions associated with solute atoms having surface area exposed to the surrounding medium. The underlying framework of the models, including the charge models used for the electrostatics, and some of the models' most recent extensions are summarized in this report. In addition, selected applications to environmental chemistry problems are presented.

Subproject no. 6: Electrochemistry and Integrated Tools Software

Single-Ion Solvation Free Energies and the Normal Hydrogen Electrode Potential in Methanol, Acetonitrile, and Dimethyl Sulfoxide
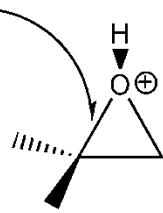
Casey P. Kelly, Christopher J. Cramer and Donald G. Truhlar

The division of thermodynamic solvation free energies of electrolytes into contributions from individual ionic constituents is conventionally accomplished by using the single-ion solvation free energy of one reference ion, conventionally the proton, to set the single-ion scales. Thus, the determination of the free energy of solvation of the proton in various solvents is a fundamental issue of central importance in solution chemistry. In the present article, relative solvation free energies of ions and ion-solvent clusters in methanol, acetonitrile, and dimethyl sulfoxide (DMSO) have been determined using a combination of experimental and theoretical gas-phase free energies of formation, solution-phase reduction potentials and acid dissociation constants, and gas-phase clustering free energies. Applying the cluster pair approximation to differences between these relative solvation free energies leads to values of -263.5, -260.2, and -273.3 kcal/mol for the absolute solvation free energy of the proton in methanol, acetonitrile, and DMSO, respectively. The final absolute proton solvation free energies are used to assign absolute values for the normal hydrogen electrode potential and the solvation free energies of other single ions in the solvents mentioned above.

Subproject no. 7: Methodology and Integrated Tools Software

How Well Can New-Generation Density Functional Methods Describe Protonated Epoxides Where Older Functionals Fail?

Yan Zhao, and Donald G. Truhlar

Predicted bond length (Å)

Method	Value
B3LYP	1.790
CCSD	1.599
M05	1.602
M05-2X	1.607
MP2	1.598
TPSSh	1.661

Basis set: 6-311++G(d,p)

In a recent article, Carlier et al. (*J. Org. Chem.* **2006**, *71*, 1592) examined the prediction of several DFT functionals and showed that the most popular density functional, B3LYP, and 15 others fail badly for the prediction of the structure of protonated 2-methyl-1,2-epoxypropane. In this note, we compare the performance of several recently developed density functionals for the calculation of structures and energetics of protonated cyclic ethers, including epoxides. We found that several of the newly developed DFT methods perform better than B3LYP or any of the other 17 functionals examined by Carlier. We conclude that a recently published functional,

M05-2X, has greatly improved performance for an unsymmetrical protonated epoxide, and we recommend this functional for studies that involve protonated epoxides and protonated ethers.

Subproject no. 8: Methodology and Integrated Tools Software

Benchmarking Approximate Density Functional Theory for s/d Excitation Energies in 3d Transition Metal Cations

Nathan E. Schultz, Yan Zhao, and Donald G. Truhlar

Holthausen has recently provided a comprehensive study of density functional theory for calculating the s/d excitation energies of the 3d transition metal cations. This study did not include the effects of scalar relativistic effects, and we show here that the inclusion of scalar relativistic effects significantly alters the conclusions of the study. We find, contrary to the previous study, that local functionals are more accurate for the excitation energies of 3d transition method cations than hybrid functionals. The most accurate functionals, of the 38 tested, are SLYP, PBE, BP86, PBELYP, and PW91.

Subproject no. 9: Methodology and Integrated Tools Software

Attractive Noncovalent Interactions in Grubbs Second-Generation Ru Catalysts for Olefin Metathesis

Yan Zhao, and Donald G. Truhlar
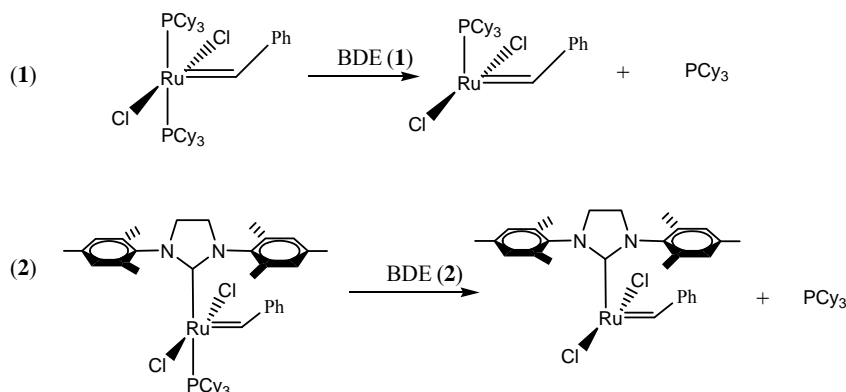
Second-generation ruthenium carbenoid catalysts for olefin metathesis are a hundred to a thousand times more active than first-generation catalysts, despite a slower initiation step. A new density functional capable of treating medium-range correlation energy shows that the relative rates of generation of the catalyst are determined by attractive noncovalent interactions.

Subproject no. 10: Methodology and Integrated Tools Software

The M06 Suite of Density Functionals for Main Group Thermochemistry, Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06 Functionals and Twelve Other Functionals

Yan Zhao and Donald G. Truhlar

We present two new hybrid meta exchange-correlation functionals, called M06 and M06-2X. The M06 functional is parametrized including both transition metals and nonmetals, whereas the M06-2X functional is a high-nonlocality functional with double the amount of nonlocal exchange (2X), and it is parametrized only for nonmetals.The functionals, along with the previously published M06-L local functional and the M06-HF full-Hartree-Fock functionals, constitute the M06 suite of complementary functionals. We assess these four functionals by comparing their performance to that of twelve other functionals and Hartree-Fock theory for 403 energetic data in 29 diverse databases, including ten databases for thermochemistry, four databases for kinetics, eight databases for noncovalent interactions, three databases for transition metal bonding, one database for metal atom excitation energies, and three databases for molecular excitation energies. We also illustrate the performance of these 17 methods for three databases containing 40 bond lengths and for databases containing 38 vibrational frequencies and 15 vibrational zero point energies. We recommend the M06-2X functional for applications involving main-group thermochemistry, kinetics, noncovalent interactions, and electronic excitation energies to valence and Rydberg states. We recommend the M06 functional for application in organometallic and inorganometallic chemistry and for noncovalent interactions.

Subproject no. 11: Methodology and Integrated Tools Software

Size-Selective Supramolecular Chemistry in a Hydrocarbon Nanoring

Yan Zhao, and Donald G. Truhlar
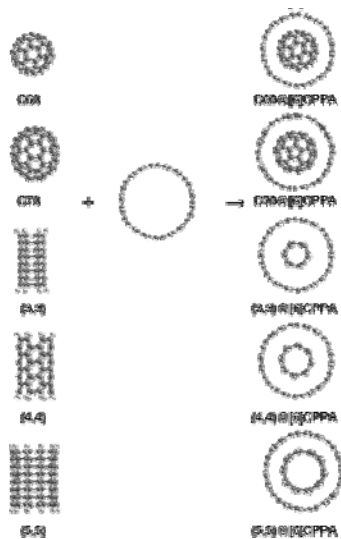
New-generation density functionals (M06-L and M06-2X) include an accurate treatment of medium-range correlation energy and have been applied to investigate host-guest interactions in supramolecular complexes in which a hydrocarbon nanoring, [6]paraphenyleneacetylene ([6]CPPA), acts as the host molecule. 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 C_{70} is bound more strongly than C_{60}.

The predicted host-guest binding energies of the (4,4), (5,5), C60, and C70 structures are 24, 43, 28, and 31 kcal/mol, respectively.

Subproject no. 12: Methodology and Integrated Tools Software

Density Functionals with Broad Applicability in Chemistry

Yan Zhao and Donald G. Truhlar

In this project we describe recent advances in the development of a new generation of density functionals with broad accuracy for main-group thermochemistry, thermochemical kinetics, noncovalent interactions, and transition metal chemistry. Several difficult cases are discussed, and the performance of the new functionals on diverse databases is presented. Recommendations are given for various application areas.

Subproject no. 13: Electrochemistry and Integrated Tools Software

Adaptive Partitioning in Combined Quantum Mechanical and Molecular Mechanical Calculations of Potential Energy Functions for Multiscale Simulations

Andreas Heyden and Donald G. Truhlar

In many applications of multilevel/multiscale methods, an active zone must be modeled by a high-level electronic structure method, while a larger environmental zone can be safely modeled by a lower-level electronic structure method, molecular mechanics, or an analytic potential energy function. In some cases though, the active zone must be redefined as a function of simulation time. Examples include a reactive moiety diffusing through a liquid or solid, a dislocation propagating through a material, or solvent molecules in a second coordination sphere (which is environmental) exchanging with solvent molecules in an active first coordination shell. In this article, we present a procedure for combining the levels smoothly and efficiently in such systems in which atoms or groups of atoms move between high-level and low-level zones. The method dynamically partitions the system into the high-level and low-level zones and, unlike previous algorithms, removes all discontinuities in the potential energy and force whenever atoms or groups of atoms cross boundaries and change zones. The new adaptive partitioning (AP) method is compared to Rode's "hot spot" method and Morokuma's "ONIOM-XS" method that were designed for multilevel molecular dynamics (MD) simulations. MD simulations in the microcanonical ensemble show that the AP method conserves both total energy and momentum, while the ONIOM-XS method fails to conserve total energy and the hot spot method fails to conserve both total energy and momentum. Two versions of the AP method are presented, one scaling as $O(2^N)$ and one with linear scaling in N, where N is the number of groups in a buffer zone separating the active high-level zone from the environmental low-level zone. The AP method is also extended to systems with multiple high-level zones to allow, for example, the study of ions and counterions in solution using the multilevel approach.

Subproject no. 14: Electrochemistry and Integrated Tools Software

Computational Electrochemistry: The Aqueous Ru3+ | Ru2+ Reduction Potential

Pablo Jaque, Aleksandr V. Marenich, Christopher Cramer, and Donald G. Truhlar

We present results of density functional calculations for the standard reduction potential of the Ru^{3+} Ru^{2+} couple in aqueous solution. The metal cations are modeled as $[Ru(H_2O)_n]^{q+}$ surrounded by continuum solvent ($q = 2, 3$; $n = 6, 18$). The continuum model includes bulk electrostatic polarization as well as atomic surface tensions accounting for the deviation of the second or third hydration shell from the bulk. After consideration of 37 density functionals with 5 different basis sets, it has been found that hybrid and hybrid meta functionals provide the most accurate predictions for the $[Ru(H_2O)_n]^{q+}$ geometries and for the corresponding reduction potential in comparison with available experimental data. The gas-phase ionization potentials of $[Ru(H_2O)_n]^{2+}$ calculated by density functional theory are also compared to results of ab initio computations using second-order Møller-Plesset perturbation theory. The difference in solvation free energies of Ru^{3+} and Ru^{2+} varies from -10.56 to -10.99 eV for $n = 6$ and from -6.83 to -7.45 eV for $n = 18$ depending on the density functional and basis set quality. The aqueous standard reduction potential is overestimated when only the first solvation shell is treated explicitly and is underestimated when the first and second solvation shells are treated explicitly.

Subproject no. 15: Electrochemistry and Integrated Tools Software

Self-consistent Reaction Field Model for Aqueous and Nonaqueous Solutions Based on Accurate Polarized Partial Charges

Aleksandr V. Marenich, Ryan Olson, Christopher Cramer, and Donald G. Truhlar

A new universal continuum solvation model (where "universal" denotes applicable to all solvents), called SM8, is presented. It is an implicit solvation model, also called a continuum solvation model, and it improves on earlier SM*x* universal solvation models by including free energies of solvation of ions in nonaqueous media in the parametrization. SM8 is applicable to any charged or uncharged solute composed of H, C, N, O, F, Si, P, S, Cl, and/or Br 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 group; all parameters are unique and continuous functions of geometry. It may be used with any level of electronic structure theory as long as accurate partial charges can be computed for that level of theory; we recommend using it with self-consistently polarized Charge Model 4 or other self-consistently polarized class IV charges, in which case analytic gradients are available. The model separates the observable solvation free energy into two components: the long-range bulk electrostatic contribution arising from a self-consistent reaction field treatment using the generalized Born approximation for electrostatics is augmented by the non-electrostatic contribution arising from short-range interactions between the solute and solvent molecules in the first solvation shell. The cavities for the electrostatic calculation are defined by superpositions of nuclear-centered

spheres whose sizes are determined by intrinsic atomic Coulomb radii. The radii used for aqueous solution are the same as parametrized previously for the SM6 aqueous solvation model, and the radii for nonaqueous solution are parametrized by a training set of 220 bare ions and 21 clustered ions in acetonitrile, methanol, and dimethyl sulfoxide. The non-electrostatic terms that are proportional to the solvent-accessible surface areas of the atoms of the solute have been parameterized using solvation free energies for the training set of 2346 solvation free energies for 318 neutral solutes in 90 nonaqueous solvents and water and 143 transfer free energies for 93 neutral solutes between water and 15 organic solvents. The model is tested with three density functionals and with four basis sets: 6-31+G(d,p), 6-31+G(d), 6-31G(d), and MIDI!6D. The SM8 model achieves the mean unsigned errors of $0.5-0.8$ kcal/mol in the solvation free energies of tested neutrals and the mean unsigned errors of $2.2-7.0$ kcal/mol for ions. The model outperforms the earlier SM5.43R and SM7 universal solvation models as well as the default Polarizable Continuum Model (PCM) implemented in *Gaussian 98/03*, the conductor-like PCM as implemented in *GAMESS*, *Jaguar*'s continuum model based on numerical solution of the Poisson equation, and the GCOSMO model implemented in *NWChem*.

Subproject no. 16: Electrochemistry and Integrated Tools Software

Charge Model 4 and Intramolecular Charge Polarization

Ryan Olson, Aleksandr V. Marenich, Christopher Cramer, and Donald G. Truhlar

Partial atomic charges provide the most widely used model for molecular charge polarization, and Charge Model 4 (CM4) is designed to provide partial atomic charges that correspond to an accurate charge distribution, even though they may be calculated with polarized double zeta basis sets with any density functional. Here we extend CM4 to six additional basis sets, and we present a model (CM4M) that is individually optimized for the M06 suite of density functionals for ten basis sets. These charge models yield class IV partial atomic charges by mapping from those obtained with Löwdin or redistributed Löwdin population analyses of density functional electronic charge distributions. CM4M/M06-2X/6–31G(d)//M06-2X/6–31+G(d,p) partial atomic charges are calculated for ethylene, CHnCl4-n (n = 0 – 4), benzene, nitrobenzene, phenol, and fluoromethanol and used to discuss gas-phase polarization effects.

Subproject no. 17: Electrochemistry and Integrated Tools Software

Polarization Effects in Aqueous and Nonaqueous Solutions

Aleksandr V. Marenich, Ryan Olson, Christopher Cramer, and Donald G. Truhlar

Polarization effects in aqueous and nonaqueous solutions were analyzed for seven neutral and three charged organic solutes by the SM8 universal implicit solvation model and class IV partial atomic charges based on Charge Model 4M (CM4M) with the M06-2X density functional. The CM4M partial atomic charges in neutral and ionic solutes and in the corresponding clustered solutes (supersolutes), which included one solute molecule and one or two solvent molecules, were modeled in three solvents (benzene, methylene chloride, and water) and compared to those in the gas phase. The use of the supersolute approach (microsolvation) allows one to account for

charge transfer from the solute to the solvent, and we find charge transfers as large as 0.06 a. u. for neutral solutes (pyridine in water) and 0.32 a. u. for ions (methoxide anion in water). Relaxation of the electronic structure of the solute in the presence of solvent increased the polarization free energy of the neutral solutes studied here, on average, by 16% in benzene, 30% in methylene chloride, and 43% in water. The increase for the ions in water averaged 43%.

Subproject no. 18: Methodology and Integrated Tools Software

A Foundation for Graphene Material Simulation: Sturctures and Interaction Potentials of Coronene Dimers

Yan Zhao and Donald G. Truhlar

In this 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-diplaced 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.

Subproject no. 19: Methodology and Integrated Tools Software

Benchmark data of Interactions in the Zeolite Model Complexes and their Use for Validation of Electronic Structure Methods

Yan Zhao and Donald G. Truhlar

Benchmark binding energies for four noncovalent and one covalent zeolite model complexes 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-pVXZ basis sets for X = D and T and separate extrapolation of the Hartree-Fock and correlation. Final stabilization energies (kcal/mol) are in the range of 3.5~19.5 kcal/mol and they were used as reference data to test six wavefunction methods and 41 DFT methods. 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 accurately describe the interactions in these zeolite model systems, one needs to use a basis set at least the size of aug-cc-pVTZ in conjunction with counterpoise corrections. Among the tested density functionals, M06-L/6-31+G(d,p) gives an mean unsigned error (MUE, without counterpoise correction) of 0.87 kcal/mol. With counterpoise corrections, M06-2X and M05-2X 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 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 the four complexes of the adsoption of isobutene on a large 16T zeolite model cluster showed that M06-L, M06, M05-2X, and M06-2X are the promising quantum mechanical methods for the hybrid quantum mechanical/molecular mechanical (QM/MM) simulations of zeolites.

Subproject no. 20: Methodology and Integrated Tools Software

A conservative algorithm for an adaptive change of resolution in mixed atomistic / coarse-grained multiscale simulations

Andreas Heyden and Donald G. Truhlar

We derive a Hamiltonian and present a simulation protocol for mixed-resolution systems that allows for a change in resolution of selected groups of atoms during a molecular dynamics simulation. The Hamiltonian uses a low-resolution force field for the part of the system distant from an active site (for efficiency) and an atomistic force field for the active site and its direct environment (for accuracy). A microcanonical simulation protocol conserves energy and angular and linear momentum. The method is also applicable to simulations in other ensembles.

Subproject no. 20: Integrated Tools Software

JAGUARATE and NWCHEMRATE

Andreas Heyden and Donald G. Truhlar

JAGUARATE is developed for interfacing the POLYRATE and JAGUAR 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 JAGUAR to calculate the potential energy surface and POLYRATE for the dynamics. NWCHEMRATE is developed for interfacing POLYRATE and NWCHEM

Technology Transfer

We are making our software available over the Web. Some of the software developed on this project is already available:

1. All of the SM8 parametrizations are available in the SMXGAUSS program. This program can read a GAUSSIAN output file corresponding to a gas-phase calculation of a given solute and carry out a single-point calculation with SM6. In addition, the above program allows liquid-phase geometry optimizations and Hessian calculations to be carried out with SM8. Although SMXGAUSS requires only a GAUSSIAN output file to perform SM8 calculations, users that have a GAUSSIAN03 executable can use SMXGAUSS in conjunction with the powerful geometry optimizers available in GAUSSIAN. For non-GAUSSIAN users, the CM4 and SM8 parametrizations are also available in the GAMESSPLUS and HONDOPLUS software programs.

2. The M05-class and M06-class functionals have been implemented in GAUSSIAN03, NWCHEM, JAGUAR, ADF, and Q-CHEM.

3. In collaboration with our coworkers at the University of Colorado at Denver, the QMMM program has been updated to include the newly developed QM/MM scheme.

4. Two new programs, JAGUARATE and NWCHEMRATE, have been developed to interface the POLYRATE program to Jaguar and NWChem, respectively.

All of these locally developed programs are available free of charge, and can be downloaded from our website, http://comp.chem.umn.edu/software.

Refereed Journal Articles, since start of project

1. "Improved Density Functionals for Water," E. E. Dahlke and D. G. Truhlar, J. Phys. Chem. A **109**, 15677-15683 (2005).
2. "Exchange-Correlation Functional with Broad Accuracy for Metallic and Nonmetallic Compounds, Kinetics, and Noncovalent Interactions," Y. Zhao, N. E. Schultz, and D. G. Truhlar, J. Chem. Phys. **123**, 161103/1-4 (2005). (communication)
3. "Density Functional for Inorganometallic and Organometallic Chemiostry," N. E. Schultz, Y. Zhao, and D. G. Truhlar, J. Phys. Chem. A **109**, 11127-11143 (2005).
4. " Design of Density Functionals by Combining the Method of Constraint Satisfaction with Parametrization for Thermochemistry, Thermochemical Kinetics, and Noncovalent Interactions," Y. Zhao, N. E. Schultz, and D. G. Truhlar, J. Chem. Theory Comput. **2**, 364 (2006)
5. "Comparative DFT Study of van der Waals Complexes: Rare-Gas Dimers, Alkaline-Earth Dimers, Zinc Dimer, and Zinc-Rare-Gas Dimers," Y. Zhao and D. G. Truhlar, J. Phys. Chem. A. **110**, 5121 (2006)
6. "Comparative Assessment of Density Functional Methods for $3d$ Transition-Metal Chemistry," Y. Zhao and D. G. Truhlar, J. Chem. Phys. **124**, 224105 (2006).
7. "Assessment of Model Chemistries for Noncovalent Interactions," Y. Zhao and D. G. Truhlar, J. Chem. Theory Comput. **2**, 1009 (2006).
8. "Predicting Aqueous Free Energies of Solvation as Functions of Temperature," A. C. Chamberlin, C. J. Cramer, and D. G. Truhlar, J. Phys. Chem. B, **110**, 5665 (2006).
9. "Adding Explicit Solvent Molecules to Continuum Solvent Calculations for the Calculation of Aqueous Acid Dissociation Constants," C. P. Kelly, C. J. Cramer, D. G. Truhlar, Journal of Physical Chemistry A **110**, 2493-2499 (2006).

10. "Aqueous Solvation Free Energies of Ions and Ion-Water Clusters Based on An Accurate Value for the Absolute Aqueous Solvation Free Energy of the Proton," C. P. Kelly, C. J. Cramer, and D. G. Truhlar, Journal of Physical Chemistry B **110**, 16066-16081 (2006).

11. "Assessment of Density Functionals for π Systems: Energy Differences between Cumulenes and Poly-ynes, Proton Affinities, Bond Length Alternation, and Torsional Potentials of Conjugated Polyenes, and Proton Affinities of Conjugated Schiff Bases ," Y. Zhao and D. G. Truhlar, Journal of Physical Chemistry A **110**, 10478-10486 (2006).

12. "Multi-Configuration Molecular Mechanics Based on Combined Quantum Mechanical and Molecular Mechanical Calculations," H. Lin, Y. Zhao, O. Tishchenko, and D. G. Truhlar, Journal of Chemical Theory and Computation **2**, 1237-1254 (2006).

13. "Pd_nCO (n = 1,2): Accurate Ab Initio Bond Energies, Geometries, and Dipole Moments and the Applicability of Density Functional Theory for Fuel Cell Modeling," N. E. Schultz, B. F. Gherman, C. J. Cramer, and D. G. Truhlar , Journal of Physical Chemistry B **110**, 24030-24036 (2006).

14. "A New Local Density Functional for Main Group Thermochemistry, Transition Metal Bonding, Thermochemical Kinetics, and Noncovalent Interactions" Y. Zhao, D. G. Truhlar, Journal of Chemical Physics **125**, 194101/1-18 (2006).

15. "A Density Functional Theory that Accounts for Medium-Range Correlation Energies in Organic Chemistry," Y. Zhao and D. G. Truhlar, Organic Letters **8**, 5753-5755 (2006).

16. "Density Functional for Spectroscopy: No Long-Range Self-Interaction Error, Good Performance for Rydberg and Charge-Transfer States, and Better Performance on Average than B3LYP for Ground States," Y. Zhao, and D. G. Truhlar, Journal of Physical Chemistry A **110**, 13126-13130 (2006).

17. "Density Functionals for Noncovalent Interaction Energies of Biological Importance," Y. Zhao and D. G. Truhlar, Journal of Chemical Theory and Computation **3**, 289-300 (2007).

18. "Single-Ion Solvation Free Energies and the Normal Hydrogen Electrode Potential in Methanol, Acetonitrile, and Dimethyl Sulfoxide", C.P. Kelly, C.J. Cramer, and D.G. Truhlar, Journal of Physical Chemistry B **111**, 408-422 (2007).

19. "How Well Can New-Generation Density Functional Methods Describe Protonated Epoxides Where Older Functionals Fail?" Y. Zhao and D. G. Truhlar, Journal of Organic Chemistry **72**, 295-298 (2007).

20. "Adaptive Partitioning in Combined Quantum Mechanical and Molecular Mechanical Calculations of Potential Energy Functions for Multiscale Simulations," A. Heyden, H. Lin, and D. G. Truhlar, Journal of Physical Chemistry B, **111**, 2231-2241 (2007).

21. "Computational Electrochemistry: The Aqueous $Ru^{3+} \mid Ru^{2+}$ Reduction Potential," P. Jaque, A.V. Marenich, C. J. Cramer, and D. G. Truhlar, Journal of Physical Chemistry C, **111**, 5783-5799 (2007).

22. "Specific Reaction Parametrization of the AM1/d Hamiltonian for Phosphoryl Transfer Reactions: H, O, and P Atoms," K. Nam, Q. Cui, J. Gao and D. M. York, Journal of Chemical Theory and Computation **3**, 486-504, (2007).

23. "Attractive Noncovalent Interactions in Grubbs Second-Generation Ru Catalysts for Olefin Metathesis," Y. Zhao and D. G. Truhlar, Organic Letter. **9**, 1967 (2007).

24. "QM/MM: What Have We Learned, Where are We, and Where Do We Go from Here?" H. Lin and D. G. Truhlar, Theoretical Chemistry Account **117**, 185-199 (2007).

25. "Size-Selective Supramolecular Chemistry in a Hydrocarbon Nanoring," Y. Zhao and D. G. Truhlar, Journal of the American Chemical Society, **129**, 8440 (2007).

26. "Benchmarking Approximate Density Functional Theory for s/d Excitation Energies in 3d Transition Metal Cations", N. Schultz, Y. Zhao, and D.G. Truhlar, Journal of Computational Chemistry, in press.

27. "The M06 Suite of Density Functionals for Main Group Thermochemistry, Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06 Functionals and Twelve Other Functionals," Y. Zhao and D. G. Truhlar, Theoretical Chemistry Accounts, in press.

28. "Self-Consistent Polarization of the Boundary in the Redistributed Charge and Dipole Scheme for Combined Quantum Mechanical and Molecular Mechanical Calculations," Y. Zhang, H. Lin, D. G. Truhlar, Journal of Chemical Theory and Computation, in press.

29. "Density Functionals with Broad Applicability in Chemistry," Y. Zhao and D. G. Truhlar, Accounts of Chemical Research, submitted.

30. "Self-consistent Reaction Field Model for Aqueous and Nonaqueous Solutions Based on Accurate Polarized Partial Charges," A. Marenich, R. Olson, C. P. Kelly, C. J. Cramer, and D. G. Truhlar, Journal of Chemical Theory and Computation, submitted.

31. "Charge Model 4 and Intramolecular Charge Polarization," R. M. Olson, A. V. Marenich, C. J. Cramer, and D. G. Truhlar, Journal of Chemical Theory and Computation, submitted.

32. "Polarization Effects in Aqueous and Nonaqueous Solutions," A. V. Marenich, R. M. Olson, A. C. Chamberlin, C. J. Cramer, and D. G. Truhlar, Journal of Chemical Theory and Computation, submitted.

33. "A Foundation for Graphene Material Simulation: Sturctures and Interaction Potentials of Coronene Dimers," Y. Zhao and D. G. Truhlar, Journal of the American Chemical Society, **129**, 8440 (2007).

34. "Benchmark data of Interactions in the Zeolite Model Complexes and their Use for Validation of Electronic Structure Method," Y. Zhao and D. G. Truhlar, Journal of the American Chemical Society, **129**, 8440 (2007).

Books and Chapters

"SMx Continuum Models for Condensed Phases," C. J. Cramer and D. G. Truhlar, in *Trends and Perspectives in Modern Computational Science*, Lecture Series on Computer and Computational Sciences, Vol. 6, edited by G. Maroulis and T.E. Simos (Brill Academic, Amsterdam, 2006), pp. 112-140.

"New QM/MM Models for Multi-scale Simulation of Phosphoryl Transfer Reactions in Solution" by Kwangho Nam, Jiali Gao and Darrin M. York submitted as a book chapter to the MD/Nano/Meso Symposium Proceedings Proceedings (ACS Symposium Series), R. Ross, editor.

Technical Reports

 None entered

Contributed Presentations

Truhlar, Donald G.; Lin, Hai; Tishchenko, Oksana; Zhao, Yan; Valero, Rosendo. **Interfacing electronic structure theory with dynamics.** 232nd ACS National Meeting, San Francisco, CA, United States, (2006)

Truhlar, Donald G.; Zhao, Yan; Schultz, Nathan E.; Dahlke, Erin E.; Iron, Mark. **New semiempirical density functionals.** 232nd ACS National Meeting, San Francisco, CA, United States, (2006)

Zhao, Yan; Truhlar, Donald G.. **Benchmark study of noncovalent interactions in the zeolite model complexes and their use for validation of density functionals and force fields.** 232nd ACS National Meeting, San Francisco, CA, United States, (2006)

Truhlar, Donald G.; Kelly, Casey P.; Marenich, Aleksandr V.; Chamberlin, Adam; Smith, Jonathan M.; Jaque, Pablo; Elmasry, Natalie; Cramer, Christopher J. **Universal solvation models and their applications.**   233rd ACS National Meeting, Chicago, IL, United States, March 25-29, 2007 (2007)

Heyden, Andreas; Truhlar, Donald G.. **Adaptive partitioning in multilevel/multiscale simulations.**   233rd ACS National Meeting, Chicago, IL, United States, March 25-29, 2007 (2007)

Zhao, Yan; Truhlar, Donald G. **Density functionals for noncovalent interaction energies of biological importance.** 233rd ACS National Meeting, Chicago, IL, United States, March 25-29, 2007 (2007)

Patents

None entered

Honors
> Donald G. Truhlar

University of Minnesota Inventor Recognition Award, 2005

> for contributing to the commercialization of University inventions

American Chemical Society Peter Debye Award for Physical Chemistry, 2006

> "for fundamental contributions in the theory of chemical reaction dynamics, especially quantum mechanical scattering theory and variational transition state theory".

Lise Meitner Lectureship Award for the year 2006

"Professor Truhlar is one of the major contributors to the enormous potential of computational quantum chemistry as a research tool in chemistry, through his numerous contributions to the generation of practical methods for electronic structure, potential energy surfaces, solvent models, reaction rates, and dynamics."

Schrödinger Medal of The World Association of Theoretical and Computational Chemists, 2006

"For his outstanding contributions to the theory and computation of chemical reaction dynamics in ground and excited states."

Elected to the International Academy of Quantum Molecular Science, 2006

Members are chosen among the scientists of all countries who have distinguished themselves by the value of their scientific work and their role of pioneer or leader of a school in the broad field of the application of quantum mechanics to the study of molecules and macromolecules. The Academy's bylaws restrict the number of members younger than 65 years to 34 worldwide.

Regents Professor, University of Minnesota, 2006

Related Sponsored Work

1. Quantum Mechanical Effects in Complex Systems

   for: National Science Foundation, Chemistry Division ($663,997 for three years)

   from: 3-1-04 to: 2-28-07

   photochemistry, enzyme kinetics, and other applications of quantum mechanical methods to complex systems

2. Variational Transition State Theory

   for: U.S. Department of Energy, Office of Basic Energy Sciences ($470,000 for three years, five months)

   from: 7-1-04 to: 11-30-07

   theoretical chemical kinetics of gas-phase processes, with applications to combustion

3. Energetic Materials Designed for Improved Performance/Low Life Cycle Costs

   for: Department of Defense (Army) ($537,775 for 5 years)

   from: 6-4-02 to: 6-3-07

   development of a predictive capability for solubility of high-energy materials in supercritical fluids

4. Neuro-physical-computational Sciences Graduate Training

   for: National Institutes of Health ($2,743,635 for five years)

   from: 9-30-04 to: 9-29-09

   interdisciplinary graduate training in computational neuroscience

5. University of Minnesota Summer Bioinformatics Institute

   for: National Institute of Biomedical Imaging and Bioengineering (NIBIB/NIH)-National Science Foundation (NSF ($657,983 for three years)

   from: 1-1-03 to: 12-31-06

summer bioinformatics institute

6. Collaborative Project: Virtual Laboratory for Earth and Planetary Materials Studies
    for: National Science Foundation ($1,809,437 for four years)
    from: 9-1-04 to: 8-31-08
    development of new methods for incorporating quantum mechanical effects in simulations for earth and planetary sciences

7. The Siepmann group is currently investigating adsorption isotherms and hydrate formation in pharmaceutical solids. This work is sponsored by NSF.

8. The Siepmann group is currently investigating vapor-liquid coexistence curves using Monte Carlo simulations and Kohn-Sham density functional theory. This work is sponsored by NSF.