

Integrated Tools for Computational Chemical Dynamics
University of Minnesota and Pacific Northwest National Laboratory
Research Report: Feb. 18, 2008

Overview

The goal of this research program is to develop more powerful simulation methods and incorporate them into a user-friendly high-throughput integrated software suite for chemical dynamics. It is supported for the period 2005-2009 by the Office of Naval Research (ONR). This is a joint grant between the Chemistry Department and the Supercomputing Institute of the University of Minnesota (PI: Donald G. Truhlar) and Pacific Northwest National Laboratory (co-PI: Bruce C. Garrett).

The University of Minnesota faculty investigators: Donald G. Truhlar, J. Ilja Siepmann, Christopher Cramer, Jiali Gao, and Darrin York. Re Pacific Northwest National Laboratory investigators: Bruce C. Garrett, Michel Dupuis, Shawn Kathmann, Greg Schenter, and Marat Valiev. Currently the project manager is Dr. Aleksandr Marenich at the University of Minnesota, and the co-manager is Dr. Marat Valiev at Pacific Northwest National Laboratory.

This research program consists of three subprojects: computational electrochemistry, heterogeneous catalysis, and computational photochemistry.

Financial

We expect no problems with reference to financial execution, but we request a time extension because local accounting services can be slow, and we need time for all financial transactions to clear. We do not anticipate that we will have unspent funds.

Scientific accomplishments to date

We have focused on addressing the challenges of accurately treating both the energetics and dynamics of molecular processes in condensed phases. The project has three subareas: computational electrochemistry, heterogeneous catalysis, and computational photochemistry, each of which involves development of integrated software for a particular area of condensed-phase chemistry. This includes tools for calculating reaction rate and transport properties and for investigating energetic materials, catalysis, and ultrafast 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 example, oxidation-reduction 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. Particular attention was paid to the development of new adaptive schemes based on treating a part of the system at a high level and a part at a low level, but where the boundary

location is function of time. The algorithms we have 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.

We have achieved advances in the following areas:

- next generation density functional theory – new, more broadly applicable functionals
- coupled cluster methods - for ground and excited states
- hybrid methods including combined quantum mechanical and molecular mechanical methods
- temperature-dependent solvation models for aqueous and nonaqueous systems
- electrostatically embedded many-body expansion
- multiconfiguration molecular mechanics
- direct calculations of diabatic representations of electronic states

We take advantage of these new representations of potential energy surfaces by interfacing them to dynamical and statistical mechanics methods, including advances in the following areas:

- optimizations in extended systems
- potentials of mean force for general reaction pathways
- nonadiabatic dynamics
- grand canonical Monte Carlo simulations
- adaptive partitioning
- solvent shifts of electronic excitations

Navy/DoD interactions, transitions (e.g., new code incorporated into generally available programs, demonstrations of code), and measurable impact

The project was designed to enable ONR and other national researchers to take advantage of new computer hardware and algorithms to meet critical needs in chemical research by developing computational chemistry software for scientific discovery by modeling and simulation. At this time we have already made significant progress in the incorporation of new codes into generally available programs.

The Minnesota density functionals (the M05 and/or M06 family of functionals) are now available in the following codes:

- Amsterdam density functional package
- Gaussian 03
- HONDOPLUS
- Jaguar
- NWChem

- Q-Chem 3.1

The Minnesota density functionals outperform many other functionals (for instance, the most popular functional, B3LYP) on several difficult cases involving main-group thermochemistry, noncovalent interactions of importance for soft materials, weakly bound complexes, and steric effects, multireference rearrangements, reactions where both organic and transition-metal bonds are formed or broken, problems, barrier heights, conformational energy, and the trend in bond dissociation energies of Grubbs' ruthenium catalysts for olefin metathesis.

During phase I, we have finalized the new universal continuum solvation model (where "universal" denotes applicable to all solvents) called SM8. The SM8 model achieves mean unsigned errors of 0.5–0.8 kcal/mol in the solvation free energies of a diverse set of tested neutral molecules and mean unsigned errors of 2.2–7.0 kcal/mol for ions with respect to available experimental data. The model substantially improves on earlier models of the SM x family and it outperforms the default continuum solvation methods implemented in *Gaussian 03*, *GAMESS*, *Jaguar*, and *NWChem*.

The SM8 model has been already incorporated into two major computational codes:

- *Gaussian 03* as the *MN-GSM* solvation module
- *GAMESS* as *GAMESSPLUS*

We have made significant progress in the development of new hybrid methodologies for the description of complex chemical transformations in the condensed phase. These methods take full advantage of parallel hardware and provide thermodynamically relevant quantities at a level of accuracy not possible before. Accurate description of potential energy surfaces is achieved by means of combined quantum-mechanical molecular mechanical (QM/MM) algorithms, including both density-functional and high-level coupled cluster methodologies. The thermal effects of the classical ("solvent") environment are taken into account using a double perturbation approach where the major part of the statistical averaging uses an effective classical representation of the system that is more efficient to compute than the real Hamiltonian. During phase I we used these ideas to implement efficient parallel computational modules for the calculations of Potential of Mean Force (PMF) and solvatochromic shifts. These modules are released as part of *NWChem* and have been benchmarked on several important applications.

Plan for the option years and code availability

We will continue our work on the development of density functionals. It will include:

- implementation of the M06-class functionals in plane wave codes
- application of the M06-class functionals for heterogeneous catalysis simulations

In the areas of computational electrochemistry and photochemistry, we plan the following:

- extension of the generalized Born approximation used in the SM8 solvation model to excited electronic states (e. g., for modeling solvatochromism)
- parametrization of models based on the nonlinear Poisson equation for electrostatics and the cavity-dispersion-solvent-structure formalism previously developed for the models using the general Born approximation

- incorporation of our solvation models into popular computational programs that will extend them to the general community of environmental chemists and Department of Defense scientists and all those interested in the accurate treatment of solvation effects

We also will continue our work in the area of hybrid multiscale type of approaches that combine different theoretical models to provide the best possible solution to a given problem. These developments will include

- further improvements in combined coupled cluster molecular mechanics approaches, in particular with respect to electron transfer processes
- implementation of new fragment based or embedding approaches where the entire system will be described quantum-mechanically for both cluster and periodic systems
- extension of free energy QM/MM methods to alchemical perturbations, including calculations of redox potentials and binding free energies

Finally we are studying the activated diffusion of hydrocarbons in zeolites as a test problem.

Project meetings over the first phase of the grant

- The PI and co-PI held a project planning meeting at the National ACS Meeting in March 2005.
- The PI and co-PI held a project planning meeting at the National ACS Meeting in August 2005.
- Marat Valiev (PNNL) visited the University of Minnesota on October 27-28, 2005
- The PI and co-PI held a project planning meeting at the National ACS Meeting in March 2006.
- Yan Zhao (University of Minnesota) visited PNNL on January 24-26, 2007.
- Alek Marenich, Ryan Olson, and Yan Zhao (University of Minnesota) visited PNNL on October 1-3, 2007.
- Bruce Garrett and Marat Valiev of PNNL and Alek Marenich, Ryan Olson, and Yan Zhao of the University of Minnesota attended the ONR meeting on PDM Fuels Cells & PDM Chemical Dynamics in Arlington on October 17-18, 2007.
- Michel Dupuis (PNNL) and Donald G. Truhlar (University of Minnesota) organized and hosted an international conference on Computational Electrochemistry at the Boston National ACS Meeting, August 2007; the symposium featured 25 speakers from six countries, including participation by Brett Dunlap from the Naval Research Laboratory and Doug Dudis and Todd Yeates from the Air Force Research Laboratory.

Web site for further information

<http://comp.chem.umn.edu/itccd/>