Summary of the Phase I review for ONR N00014-05-1-0538:

Integrated Tools for Computational Chemical Dynamics

Department of Chemistry, University of Minnesota

and

Chemical & Materials Sciences Division and Environmental Molecular Sciences
Laboratory, Pacific Northwest National Laboratory

The goal of this project is to develop 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

The research areas addressed by this project are:

- Computational Electrochemistry: thermochemistry and kinetics of redox processes (e.g., redox potentials and electron/hole transport)
- Heterogeneous Catalysis: thermochemistry and kinetics of interfacial reaction processes (e.g., adsorption and/or diffusion of the reactants to the active site, catalytic conversion at the active site, and desorption and/or diffusion of products from the active side)
- Computational Photochemistry: energetics and dynamics of electronically excited states (e.g., solvatochromatic shifts, nonadiabatic coupling and dynamics)

We focus on addressing the challenges of accurately treating both the energetics and dynamics of molecular processes in *condensed phases*. Classical or molecular mechanics (MM) potentials are efficient for condensed phase simulations but inadequate to treat chemical reactions. Accurate energetics, particularly to reactions, require high-order electronic structure methods (i.e., with N^6 scaling or higher) and present a major challenge for condensed phases systems. New approaches are needed that allow high-order electronic structure calculations to be performed for condensed phase systems. Dynamics calculations for reactions in condensed phases generally constrain the description of the reaction pathway. As an example, reaction pathways for solution phase reactions are often assumed to be prescribed reaction coordinates, such as bond distances, of the reaction pathway for the gas-phase process. New tools are required that allow for more general descriptions of reaction pathway, incorporating motions of the parts of the system, including solvent reorganization, that influence the reaction rates. In addition, accurate kinetics and thermodynamics requires sufficient sampling over environmental variables, often while employing ab initio electronic structure methods for the energetics. The requirement to accurately treat both the energetics and the statistical mechanics is a major challenge.

In phase I, we have made significant progress in methods for calculating energetics, dynamics, and their integration for condensed phase processes. Our approach to energetics is to build on existing electronic structure methods to develop efficient representations of potential energy surfaces and includes 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 QM/MM, temperature-dependent solvation models for aqueous and nonaqueous systems, Electrostatically embedded many-body expansion (EE-MB), and multiconfiguration molecular mechanics (MCMM)
- Direct calculations of diabatic representations of electronic states

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

- Optimizations in extended systems
- Potentials of mean force (PMFs) for general reaction pathways
- Non-adiabatic dynamics
- Grand Canonical Monte Carlo simulations
- Adaptive partitioning (flexible QM region)
- Solvent shift of electronic excitations

We will present technical details in this review in the following four areas.

- Advances in New Density Functionals for Computational Chemical Dynamics (shortcomings and limitations of popular functionals, constraints and parametrization, performance and future plan)
- Solvation Models and Computational Electrochemistry (parametrization and performance of SM8, and theoretical prediction of reduction potentials in solution)
- Hybrid Methods for Studies of Chemical Processes in Condensed Phase (QM/MM methods based on coupled cluster theory, structural optimizations with QM/MM, free energy profiles for reactions in condensed phases, nudged elastic band methods for reaction pathways in condensed phases, QM/MM applications to excited states)
- Method and Code Integration (review of tools developed and programs in which they have been implemented, ongoing integration efforts and examples, ongoing and future work on Grand Canonical Monte Carlo, EE-MB, QM/MM, and adaptive partitioning)