# *At a Glance*

## Motivation

- Develop and implement highly accurate and efficient computational methods for characterizing complex chemical transformations in condensed phase environments.

## Scientific Challenge

- The numerical complexity of a quantum mechanical description presents an enormous computational challenge for proper inclusion of the effects of temperature/pressure fluctuations in large scale systems. This issue is resolved in this work using a multi-disciplinary approach where a adaptive multi-scale description is constructed to give the most accurate and efficient description of a given chemical system.
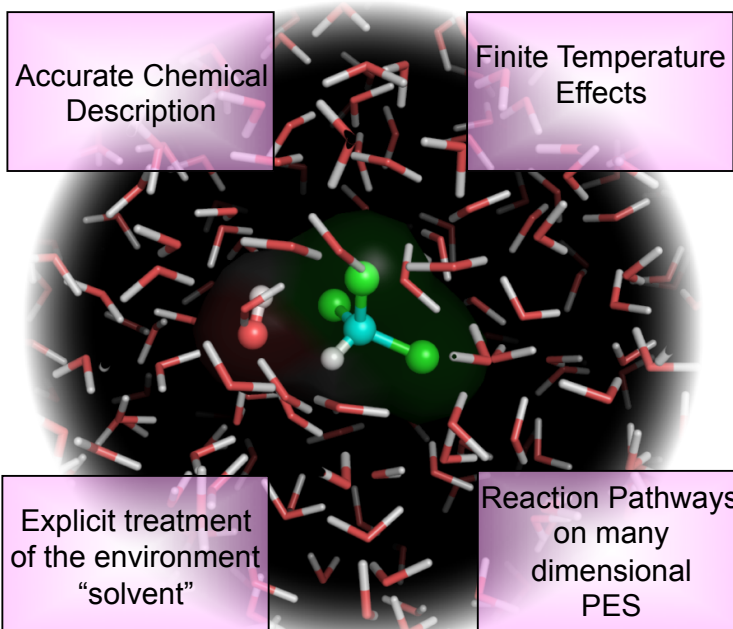
## Impact

- The developed methods have been demonstrated to provide accurate and comprehensive description for a wide range of condensed phase systems. The parallel implementation of these methods in the open source NWChem computational chemistry code ensures wide availability and deployment across different computing platforms.

## Points of Contact

ONR
Peter Schmidt
peter.schmidt1@navy.mil

Principal Investigator
Bruce C. Garrett
(509) 372-6344
bruce.garrett@pnl.gov

This effort is part of the ONR Program (grant 00014-05-01-0538) that was supported under ONR BAA 04-024 titled Research Tools Design Consortia



Accurate Chemical Description

Finite Temperature Effects

Explicit treatment of the environment "solvent"

Reaction Pathways on many dimensional PES

We have made significant accomplishments in the development of new hybrid methodologies for describing complex chemical transformation in condensed phase. These methods take full advantage of parallel hardware and provide thermodynamically relevant quantities at the level of accuracy not possible before.

Accurate description of potential energy surfaces is achieved by means of combined quantum-mechanical molecular mechanics (QM/MM), including both density-functional and high level coupled cluster electronic structure methodologies. Efficient algorithms for structural optimizations and reaction pathway determination have been developed. Free energy calculations through coupled cluster treatment of quantum effects were implemented using a multi-layered perturbation approach where the major part of the statistical averaging is shifted to an effective classical representation.

To account for dynamical re-crossing in rate calculations of chemical reactions, efficient parallel algorithms for calculating a transmission coefficient, using the reactive flux method, were developed and implemented. We explored the dependence on the transmission coefficient calculation on the initial conditions for the trajectories of the ensemble, thereby improving the sampling of the phase space and obtaining converged results with reduced simulation times.

**Key Publications:**

- Valiev, M.; Garrett, B. C.; Tsai, M.-K.; Kowalski, K.; Kathmann, S. M.; Schenter, G. K.; Dupuis, M. *J Chem Phys* **2007, 127, 051102.**
- Fan, P. D.; Valiev, M.; Kowalski, K. *Chem. Phys. Lett.* **2008, 458, 205.**

# *At a Glance*

## Motivation

- 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.

## Scientific Challenge

- We are addressing the challenges of accurately treating both the energetics and dynamics of molecular processes in condensed phases. In particular, this work involves development and improvement of theoretical models for thermochemical kinetics and rate constants, photochemistry and spectroscopy, chemical and phase equilibria, electrochemistry, and heterogeneous catalysis.

## Impact

- We have developed several highly accurate computational methods that essentially outperform older approaches. These new methods have been made available for the global chemical community by incorporating them into several major computational codes.

## Points of Contact

ONR
Peter Schmidt
peter.schmidt1@navy.mil

Principal Investigator
Donald G. Truhlar
(612) 624-7555
truhlar@umn.edu

### Density Functional Theory: Development and Integration

We have developed the Minnesota suite of density functionals that 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 Minnesota density functionals are now available in several popular computational programs, including the Amsterdam Density Functional package, GAMESS, Gaussian, NWChem, Q-Chem, and Schrodinger.

### Modeling of Solvation Effects

We have developed several advanced self-consistent reaction field continuum solvation models. These models essentially improve on earlier ones, and they are 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. These models do not require the user to assign molecular mechanics types to an atom or a group; all parameters are unique and continuous functions of geometry. The solvation models developed under the project have been incorporated into integrated software freely distributed by the University of Minnesota at *comp.chem.umn.edu* as well as into commercial codes such as Gaussian, Q-Chem, and Schrodinger.

### Thermodynamics of Associating Fluids

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. We have developed special types of Monte Carlo moves (aggregation-volume-bias Monte Carlo algorithm) that can overcome these sampling problem. These methods have been implemented into the software packages CP2K (*cp2k.berlios.de*) and MCCCS (*towhee.sourceforge.net*). Both of these packages are available via a GNU general public license.

### Quantum Mechanical/Molecular Mechanical Simulation Methods For Heterogeneous Catalysis

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 $\pi$-bonds with the catalyst surface. The work 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.

**Key Publications:**

- Y. Zhao and D. G. Truhlar, Theor. Chem. Acc. **120**, 215 (2008), Acc. Chem. Res. **41,** 157 (2008)
- A. V. Marenich, C. J. Cramer, and D. G. Truhlar, J. Phys. Chem. B **113**, 6378 (2009)