We are focusing on addressing the challenges of accurately treating both the energetics and dynamics of molecular processes in both gas and condensed phases. The project includes tools for calculating reaction rates and transport properties and for investigating energetic processes, catalysis, and dynamics. We have developed protocols for calculating relevant thermodynamic and kinetic parameters and computational software for carrying out calculations based on these protocols. We have developed an array of methods for multi-time-scale simulation. The algorithms being 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.

One of the most exciting topics in the project is the use of Minnesota density functionals in studying supra-molecular compounds. The popular B3LYP density functional and most other older functionals are inaccurate for noncovalent (for instance, aromatic-aromatic) interactions. One of the ways to improve the performance of DFT is to optimize the exchange-correlation functionals for a broad range of properties including rare-gas dimers, aromatic-aromatic interactions, and other data sensitive to medium-range correlation energy, such as barrier heights. This approach has been used for the development of the M06-2X density functional which has been validated for \( \pi \ldots \pi \) stacking and has also been employed to study supramolecular assembly involving a nanoring and to study the dimerization of coronene as a model for interacting graphene sheets in multiwalled carbon-based assemblies.

We have developed a new charge-density based solvation model called SMD. The SMD algorithm involves an integration of the nonhomogeneous Poisson equation for electrostatics. The model has been parameterized using a large training set of neutral and ionic solvation free energies for various solutes in water and organic solvents (nearly 3000 data). The SMD model parameters are recommended to be used for the calculation of solvation free energies within the framework of the Generalized Conductor-like Screening Model (GCOSMO) implemented in NWChem.

Another field of interest is variational transition state theory. Variational transition state theory using variable-reaction-coordinate and multifaceted dividing surfaces has been recently implemented into the POLYRATE program. This program now has capability to calculate reaction rates for barrierless association reactions. Reaction rate constants for barrierless association reactions can be calculated at canonical, microcanonical, and total energy and total angular momentum resolved microcanonical levels. We have carried out cutting edge large scale benchmark excited state calculations of the zinc-porphyrin monomer in aqueous solution using combined coupled cluster molecular mechanics formalism, in which the coupled cluster methods are equation of motion approach with singles and doubles and completely renormalized non-iterative triples corrections. Zinc-porphyrin is important in understanding photochemical properties of \( \pi \)-conjugated systems.

We are developing new potential energy functions for the study of adsorption isotherms of hydrocarbons in zeolites. The new potential energy functions are based on a combined quantum mechanical/molecular mechanical method involving adaptive partitioning so that the zone treated quantum mechanically moves with the adsorbate. We are interfacing this new potential with a Monte Carlo Gibbs ensemble algorithm to calculate the adsorption isotherms.

We are studying the structure of hydrous silica melts that is important for gaining insight into the structure of the Earth’s upper mantle that exists at the conditions (high temperatures and pressure) that make experimental studies of these systems challenging. Simulation provides an alternative means to examine their structural properties. To model hydrous silica melts at high temperatures and pressures we employ an empirical force field and Monte Carlo simulations in the isobaric-isothermal ensemble as well as first-principles molecular dynamics simulations using density functional theory.