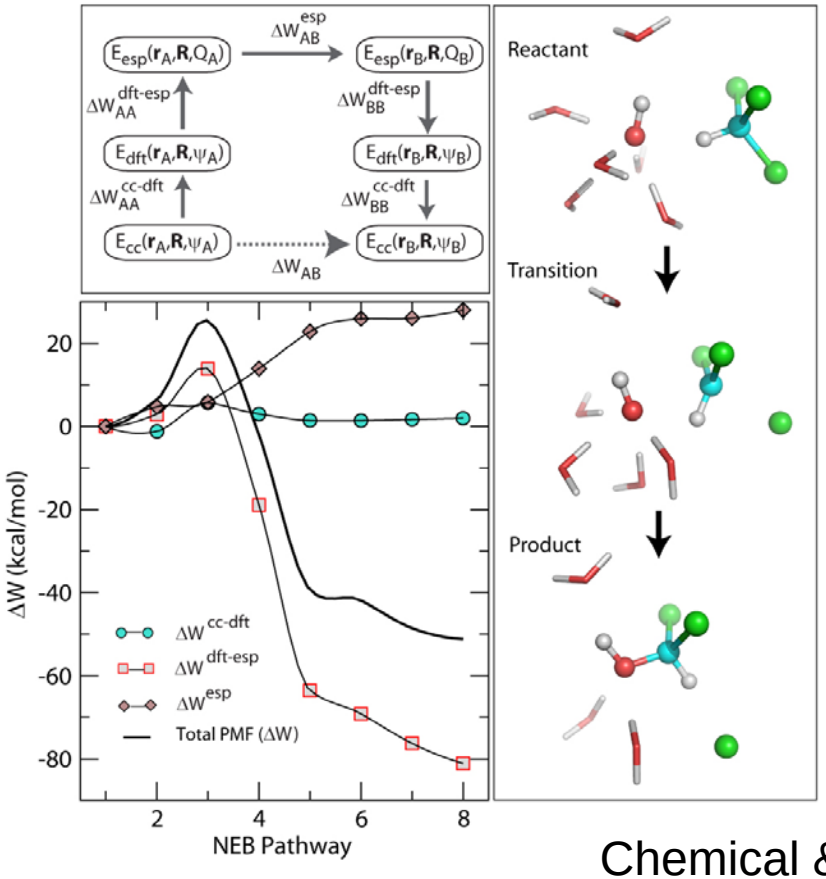
Integrated Tools for Computational Chemical Dynamics

Research Tools Design Consortium



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Goals

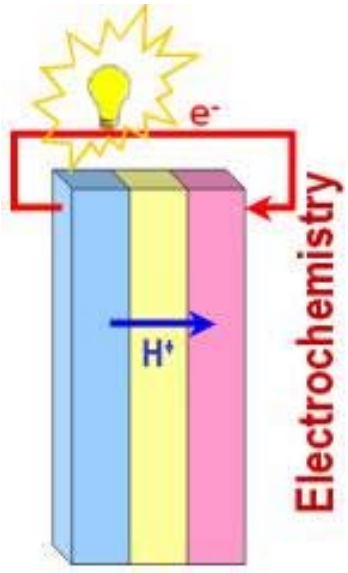
- Develop more powerful simulation methods and incorporate them into a user-friendly high-throughput integrated software suite for chemical dynamics
- Combine electronic structure packages with dynamics codes and efficient sampling algorithms for *condensed-phase* modeling of problems in the areas of:
  - thermochemical kinetics and rate constants
  - photochemistry and spectroscopy
  - chemical and phase equilibria

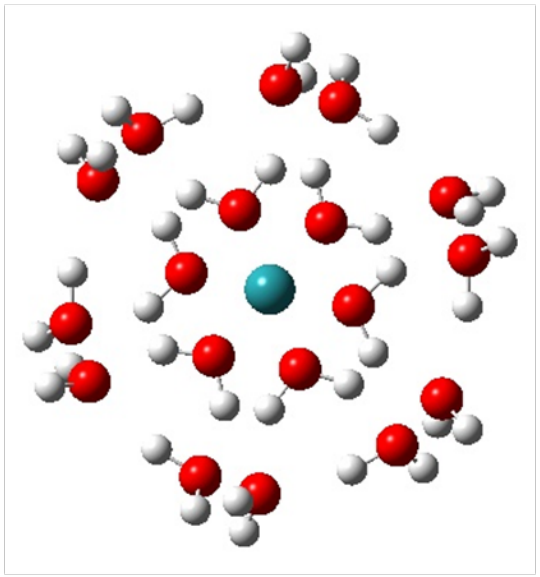
Research Areas

- Computational Electrochemistry
  - Thermochemistry and kinetics of redox processes, e.g.,
    - redox potentials
    - 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
    - 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 (e.g., conical intersections) and dynamics

Computational Electrochemistry

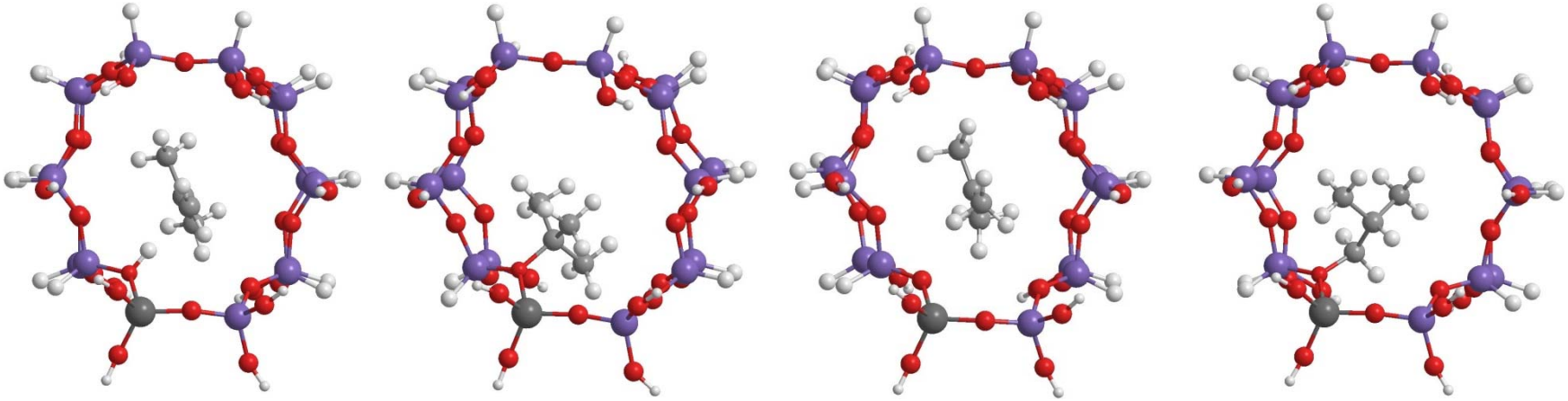
- Charge transfer processes play critical roles in
  - Reduction/oxidation of contaminants in the environment
  - electron/hole creation
  - transport for hydrogen production and fuel cells
- The sensitivity of charge transfer processes to condensed-phase surroundings presents a challenge for computational methods





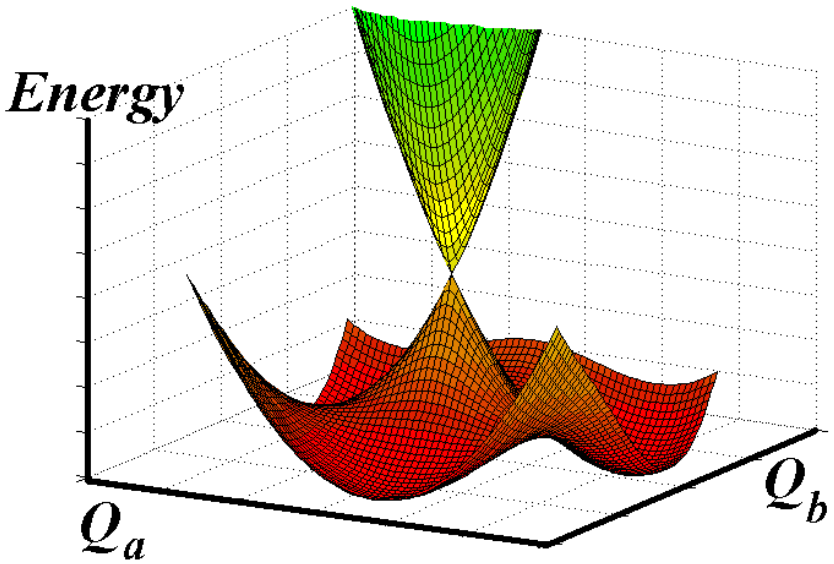
Heterogeneous Catalysis

- Catalysis is a common element in many applications areas (energy conversions, chemical synthesis, etc.)
- Molecular environment can be a major influence on reaction energetics, which requires simulation tools to adequately sample environmental variables
- Accuracy of relevant reaction energetics for condensed phase is the major limitation to the accuracy of computed rate constants and requires integration of accurate electronic structure methods with simulations



Computational Photochemistry

- Electronic excitations offer a means to control chemical processes, but require understanding radiationless de-excitation processes
- Treatment of the electronic structure and dynamics of curve crossings is challenging for gas-phase systems and a major challenge for condensed phase systems



Integrating Dynamics & Energetics

- Accurate energetics are necessary …
  - Existing electronic structure methods (e.g., DFT, Coupled Cluster, etc.) provide the foundations for computing the energetics of molecular processes
- … but not sufficient
  - New methods are required that build on this foundation and interface with the electronic structure methods to calculate physical observables
- Electronic structure has dominated computational chemistry …
  - High computational costs drive computational needs
- … and equal weight now needs to be placed on dynamics and statistical mechanics for *condensed-phase* systems
  - Getting the statistical mechanics right is an imperative; the entropic driving force competes with the energetic one, and free energies dictate thermodynamic stability and activation barriers

Challenges for Computations of Molecular Processes in *Condensed Phases*

- Energetics
  - Classical potentials (molecular mechanics) are inadequate to treat chemical reactions
  - Accurate energetics of bond-breaking/making require high-order electronic structure methods (i.e., with N^6 scaling or higher) and are difficult for condensed-phases systems
- Dynamics
  - Reaction pathways for condensed-phase processes are generally limited to un-optimized reaction coordinates
  - Accurate kinetics and thermodynamics require sufficient sampling – need to get the statistical mechanics right

Status Report on Methods Development and Implementation

- Energetics – build on existing electronic structure methods to develop efficient representations of potential energy surfaces
  - New classes of density functionals have been developed
  - Coupled cluster methods are now implemented for ground and excited states in QM/MM studies
  - Hybrid methods developed and/or implemented
    - QM/MM approaches based on high-level methods
    - T-dependent solvation models for aqueous and nonaqueous solutions
    - Electrostatically embedded many-body expansion (EE-ME)
    - Multiconfiguration molecular mechanics (MCMM)
  - Direct calculations of diabatic representation of electronic states is planned for next phase

Status Report on Methods Development and Implementation

- Dynamics and Statistical Mechanics – interface to new representations of potential energy surfaces for calculations in condensed-phase systems
  - Approach for geometry optimizations in extended systems is developed and implemented
  - Potentials of mean force (PMFs) calculations for general reaction pathways based on QM(CC)/MM calculations now possible
  - Grand canonical and Gibbs ensemble Monte Carlo methods are implemented
  - Adaptive partitioning (flexible QM region in QM/MM calculations) is developed and being implemented
  - Methods for solvatochromic shifts in progress
  - Non-adiabatic dynamics is planned for next phase

Method Integration into a Software Suite

- Modular components can be implemented in a variety of codes (NWChem, GAMESS, Jaguar, Q-Chem…)
  - Increase impact of new methods by having them available in a number of commonly used, widely accessible codes
- U of M software is a primary target
- NWChem is the primary platform for implementation in a massively parallel framework

Presentations

- Advances in New Density Functionals for Computational Chemical Dynamics – Yan Zhao
- Solvation Models and Computational Electrochemistry – Alek Marenich
- Hybrid Methods for Studies of Chemical Processes in Condensed Phase – Marat Valiev
- Methods and Code Integration – Ryan Olson