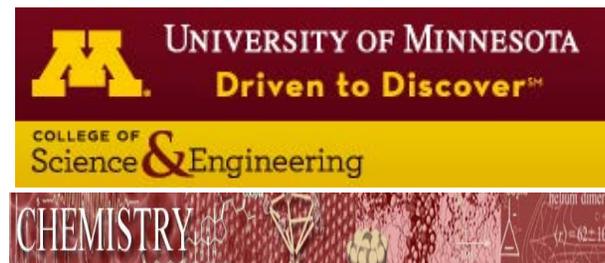


The Logo that Dare not Speak Its Name



Charge Transfer and Charge Transport in Photoactivated Systems

Developing Electron-Correlated Methods for Excited State Structure and Dynamics in the NWChem Software Suite

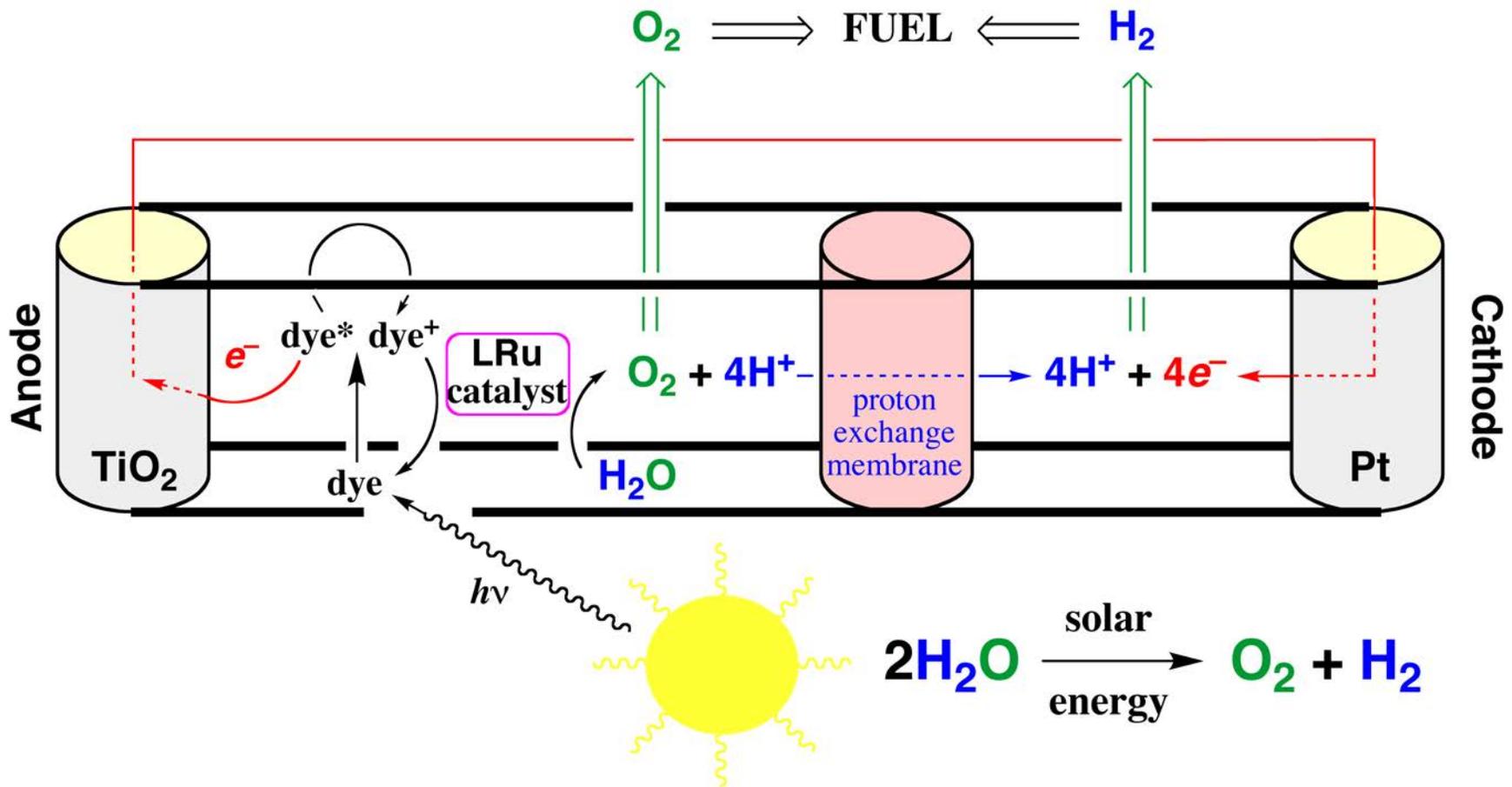
Christopher J. Cramer

SciDAC Kickoff Meeting, September 2012



Conversion of Solar Energy to Green Fuel

Schematic of the Dye-Sensitized Solar Cell



Mission and Goals

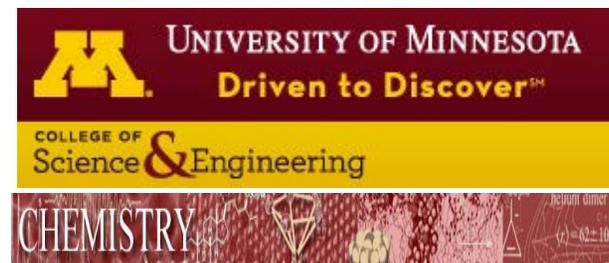
Implement a suite of methods in the NWChem software suite in order to perform electronically excited-state dynamics in solution and to provide improved capabilities for excited-state dynamics in the gas phase.

1. Multistate complete-active-space second-order perturbation theory including relativistic effects
2. State-specific non-equilibrium and equilibrium continuum solvation effects for the computation of excited-state wave functions
3. Algorithms for the treatment of electronically nonadiabatic and ultrafast dynamics in both the gas-phase and solution
4. Electrostatically embedded multiconfiguration molecular mechanics and molecular mechanics (EE-MCMM/MM) schemes
5. Multiscale approaches for the treatment of explicit *local* solvation environments with embedding to include longer-range solvent effects
6. Monte Carlo strategies for efficient conformational sampling of large and flexible chromophores

Lead Personnel

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Prof. Laura Gagliardi
Prof. J. Ilja Siepmann
Prof. Donald G. Truhlar



Pacific Northwest National Laboratory

Dr. Bert de Jong
Dr. Niri Govind



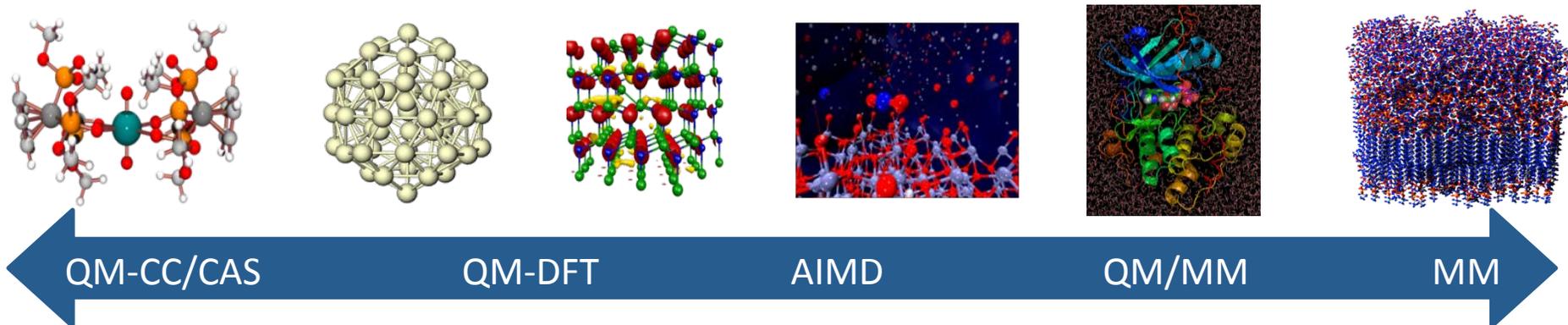
Lawrence Berkeley National Laboratory

Dr. Esmond Ng (FASTMath)
Dr. Chao Yang (FASTMath)
Dr. Leonid Olikier (SUPER)



NWChem Software Suite

A massively parallel and scalable open-source development platform for computational chemistry.



- DOE's premier computational chemistry software
- Scalable with respect to scientific challenge and compute platforms, and portable
- From molecules and nanoparticles to solid-state and biomolecular systems
- Open-source (ECL 2.0)

<http://www.nwchem-sw.org>



NWCHEM
HIGH-PERFORMANCE COMPUTATIONAL
CHEMISTRY SOFTWARE

NWChem Overview

Developed at EMSL

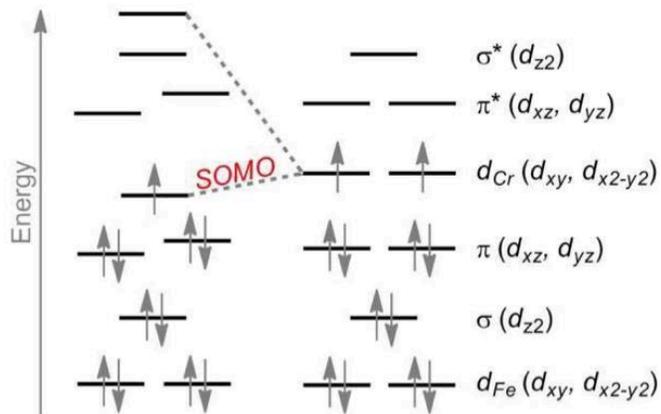
Open source since Oct 2010

- NWChem is suite of methodologies to solve large scientific problems
 - Gaussian-based DFT/TDDFT
 - Ground & Excited States, Optimization, Properties (NMR, Electric field gradient, linear response,...)
 - Plane wave based DFT
 - Car-Parinello MD (CPMD), Band Structure, Optimization, etc.
 - High Accuracy Methods → MP, CC, EOMCC
 - Ground & Excited States
 - Molecular Dynamics, Molecular Mechanics
 - Integrated Methodologies → QM/MM
 - Scripting → Python

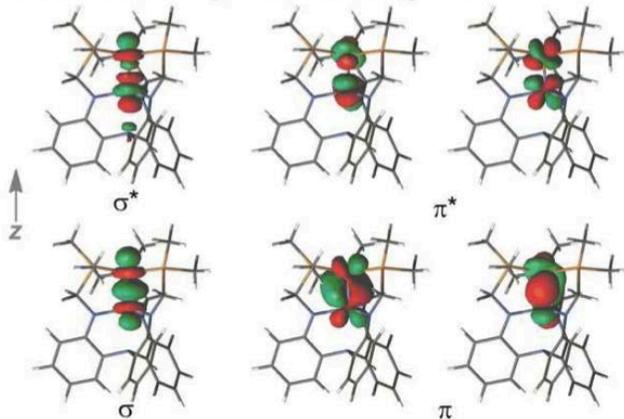
www.nwchem-sw.org

Specific Initiatives

Multistate complete-active-space second-order perturbation theory including relativistic effects



Delocalized Bonding and Anti-bonding MOs



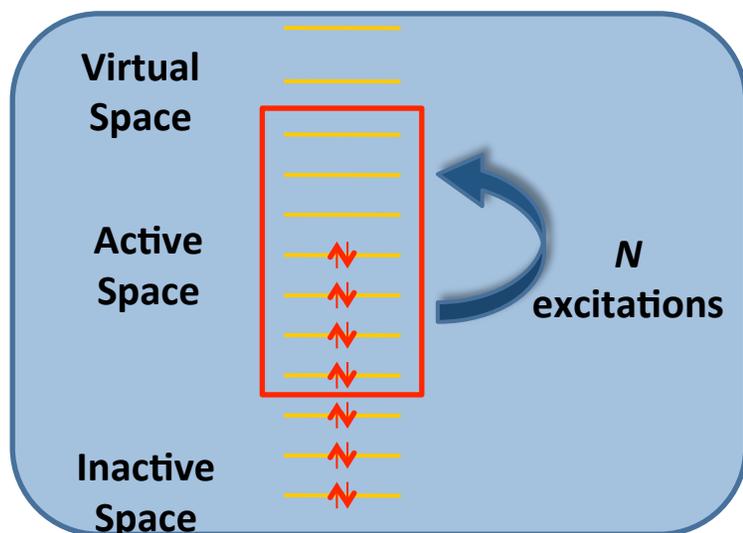
Challenge: Bond breaking, potential energy surface degeneracies, symmetry breaking problems, biradicals, organic photophysics, transition metal bonding and spectroscopy, and actinide chemistry. **Excited electronic states.**

Theory:

- Multiconfigurational complete-active-space (CASSCF) wave functions
- New wave-function models to overcome the limitations of the CASSCF approach.
- Perturbation Theory for dynamical electron correlation
- Relativistic Hamiltonians

Representative Sub-task

Algorithms for the treatment of excited electronic states



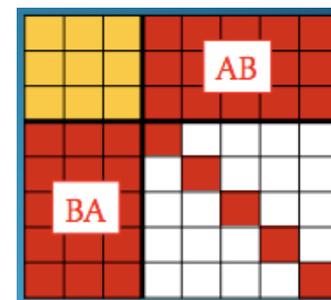
CASSCF: Full CI in the active space

RASSCF: Several Sub-Spaces with some constraints

Split-CAS: Treat explicitly only the most important configurations

Implement these methods into

NWChem program



Mathematical issue: Is there a way to get a cheaper scaling of these methods?

Scientific issue: How accurate is Split-CAS with respect to CASSCF?

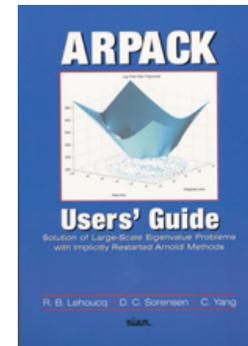
Algorithmic Issue: How can these methods be massively parallelized and benefit from modern hardware?

Representative Sub-task

Multistate complete-active-space second-order perturbation theory including relativistic effects

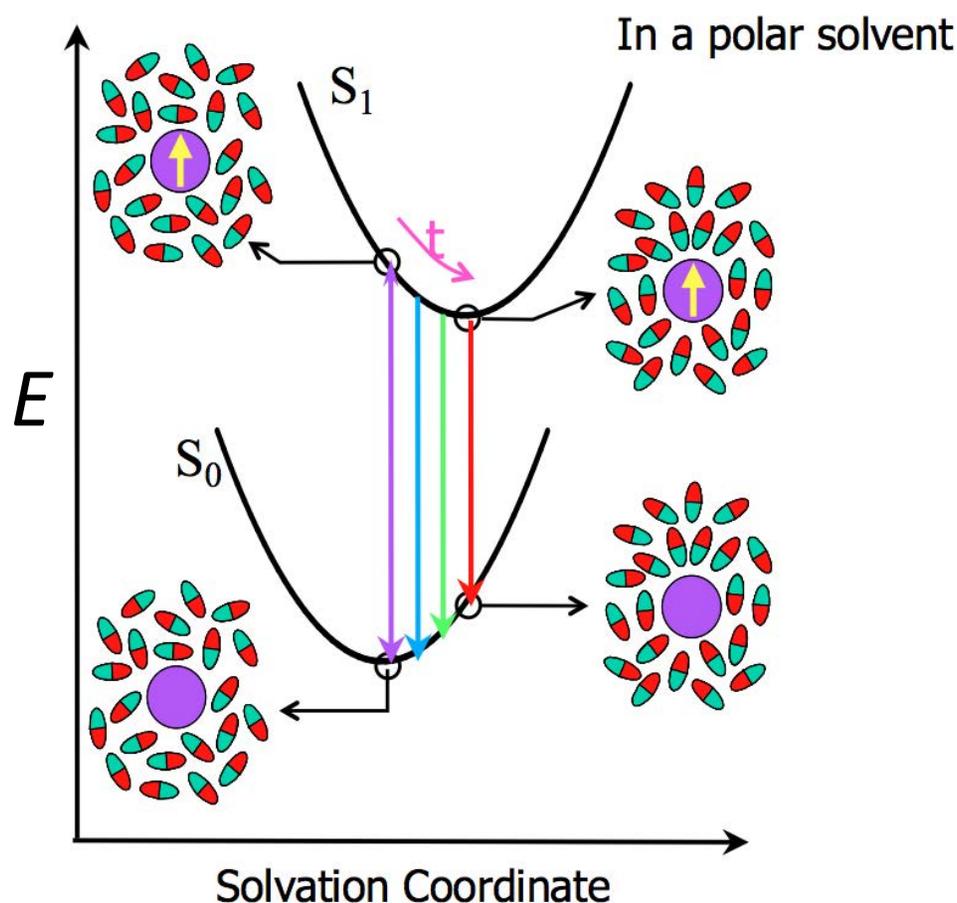
Leverage algorithms and solvers developed by FASTmath SciDAC institute to solve Large scale generalized eigenvalue problem $Hx = \lambda Sx$

- Leverage the PARPACK
 - Implicit restart
 - Shift-invert , work with $(H - \sigma S)^{-1}$
 - Need to solve linear systems of equation
- Use Jacobi-Davidson
 - Based on Newton's method
 - Solve projected linear equations to correct eigenvector approximations
- Subspace iteration
 - Increase the amount of concurrency in eigenvalue computation



Specific Initiatives

State-specific non-equilibrium and equilibrium continuum solvation effects for the computation of excited-state wave functions



Challenge: computation of excited-state wave function interacting with (evolving) inertial and dynamic components of solvent reaction field

Plan: Implement Vertical Electrostatic Model (VEM) based on Polarized Continuum Model (PCM) or Generalized Born (GB, SM9) for absorption, emission, and evolution

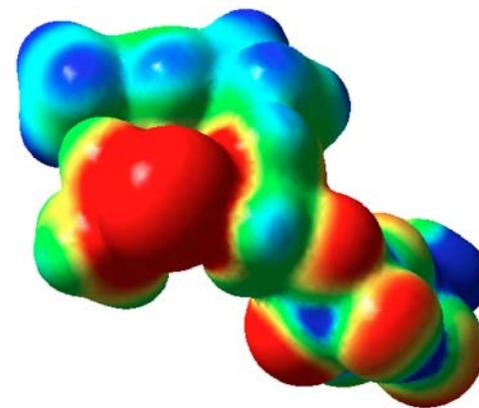
Representative Sub-task

State-specific non-equilibrium and equilibrium continuum solvation effects for the computation of excited-state wave functions

Within the SM9 VEM formalism, we need (fast) atomic Hirshfeld charges to represent solute charge distribution

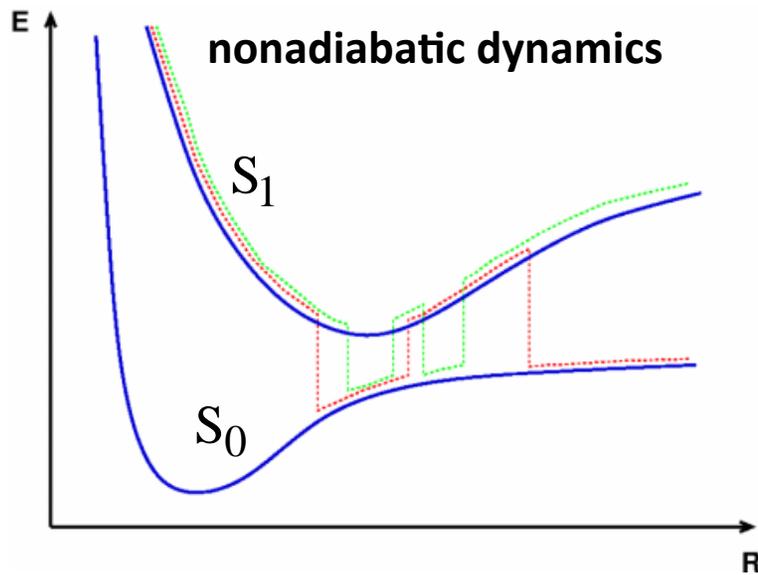
$$q_i^{\text{H}} = Z_i - \sum_j \rho(\mathbf{r}_j) \rho_{0,i}(\mathbf{r}_j) \left[\sum_k^{\text{atoms}} \rho_{0,k}(\mathbf{r}_j) \right]^{-1}$$

Details requiring attention include storage of atomic proton densities, alignment of real-space grids for arbitrary molecular geometries, and derivation/coding of derivatives of Hirshfeld charges with respect to density-matrix elements (to permit interval vs. external self-consistent reaction field schemes)



Specific Initiatives

Algorithms for the treatment of electronically nonadiabatic and ultrafast dynamics in both the gas-phase and solution



Challenge: treatment of the time dependence of fluorescence, other early-time photophysical processes, ultrafast phenomena and photochemistry requires a treatment of electronically nonadiabatic dynamics, but there is no general software package available for this kind of dynamics in both the gas-phase and solution.

Theory

- Trajectory surface hopping method with fewest-switches(FS) algorithm and time-uncertainty (TU) scheme
- Coherent switches with decay of mixing (CSDM)
- Real time Ehrenfest dynamics
- Including dynamical solvent effects

$$H\Psi(\mathbf{Q}, \mathbf{q}) = E_{\text{full}} [c_1(\mathbf{Q})\psi_1(\mathbf{q}; \mathbf{Q}) + c_2(\mathbf{Q})\psi_2(\mathbf{q}; \mathbf{Q})]$$

$$H = \sum_k^{\text{nuclei}} -\frac{1}{2m_k} \nabla_k^2 + H_{\text{el}} + V_N$$

$$\sum_k^{\text{nuclei}} \left[\frac{1}{2m_k} \nabla_k^2 + \sum_{j=1}^2 \left(2\langle \psi_i | \nabla_k | \psi_j \rangle \cdot \nabla_k + \langle \psi_i | \nabla_k^2 | \psi_j \rangle \right) \right] c_i = (E_{\text{full}} - E_i) c_i$$

Representative Sub-task

Algorithms for the treatment of electronically nonadiabatic and ultrafast dynamics in both the gas-phase and solution

ANT (Adiabatic and Nonadiabatic Trajectories) program

Two methods for non-Born-Oppenheimer dynamics:

FSTU: surface hopping by fewest switches with time uncertainty

CSDM: coherent switches with time-uncertainty



Implement FSTU with decoherence into NWChem

NWChem program

(real-time Non-Born-Oppenheimer dynamics)

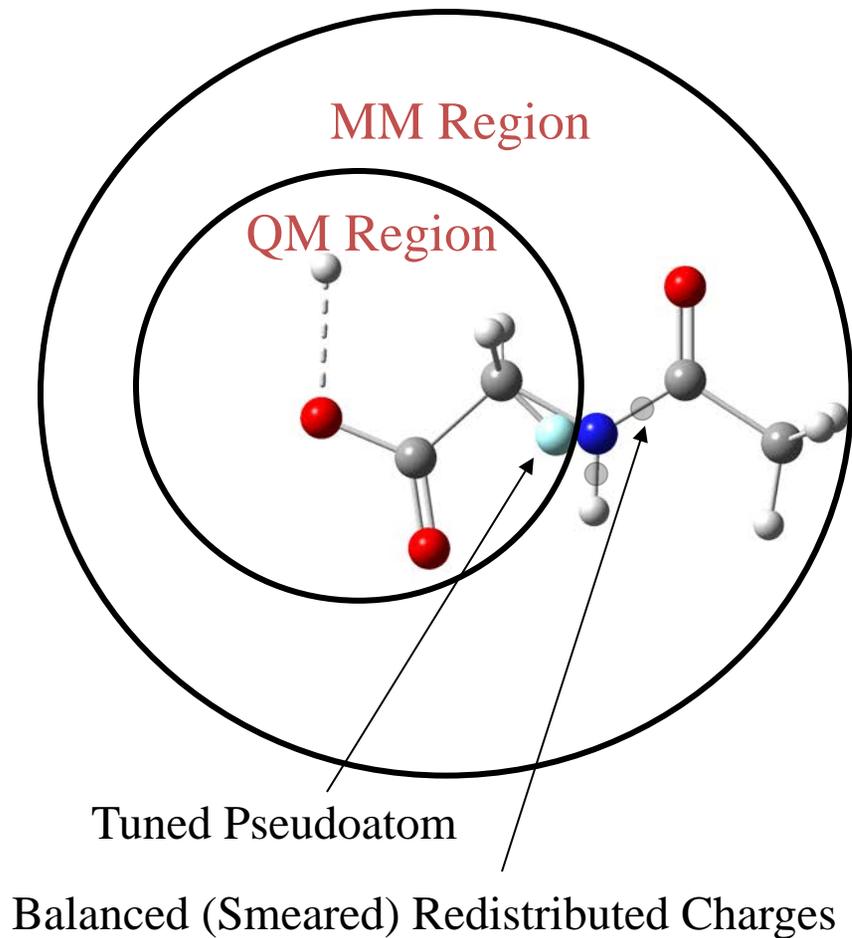
Mathematical issue: Is it physically correct to add decoherence onto FSTU?

Scientific issue: How accurate is FSTU with decoherence? Can a mean-field FSTU approach be developed for bunched excited states?

Algorithmic Issue: What is the most efficient way to integrate the coupled differential equations? What time-propagation algorithms are most efficient?

Specific Initiatives

Tuned and balanced (smeared) redistributed charge schemes in the combined quantum mechanical and molecular mechanical (QM/MM) methods



Challenge: Polar bonds across the the QM/MM boundary.

Method:

Charge Balancing: Adjust the MM charges to conserve the total charge of the entire QM/MM system.

Charge Redistribution: Move the charges that are close to the boundary away from the boundary.

Charge Smearing: Place the redistributed charges in Slater-type orbitals.

Tuned Pseudoatom: Use Fluorine as the link atom but add a pseudopotential $U(r)$ to it to mimic the original MM atom.

Representative Sub-task

Tuned and balanced (smeared) redistributed charge schemes in the combined quantum mechanical and molecular mechanical (QM/MM) methods

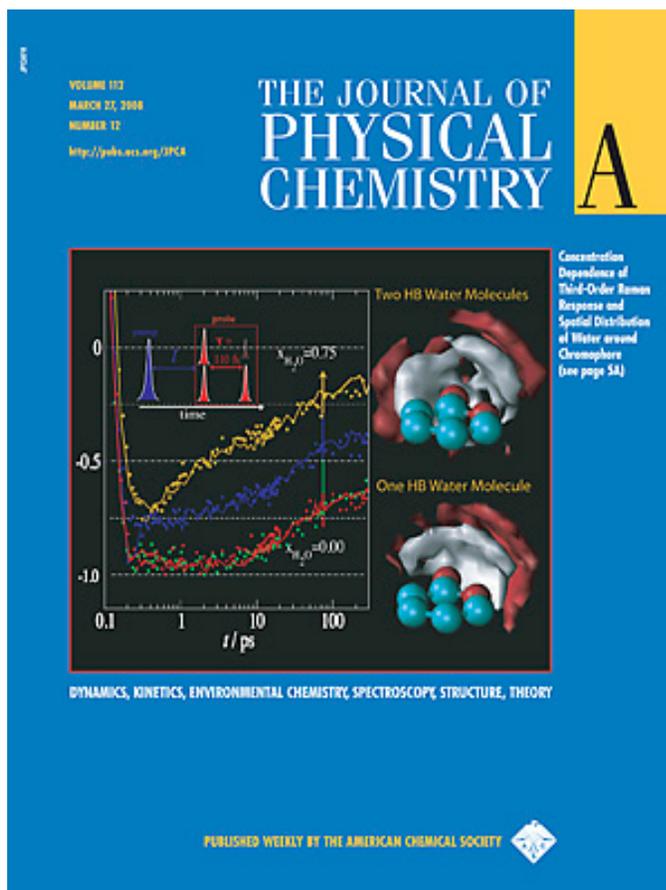
1. A code is needed to properly balance and redistribute the MM charges.
2. Within the new QM/MM schemes, the gradients and Hessians of the redistributed charges are to be partitioned on to the real QM and MM atoms.
3. A code is needed to represent the smeared charges by pseudopotentials, which can be implemented in conventional quantum mechanical calculations.

$$\rho_{\text{MM}}(r) = q_{\text{MM}} \exp(-2r/r_0)/(\pi r_0^3)$$

4. Implement the usage of the tuned pseudoatom atom, rather than the H atom, as the link atom, as well as a subroutine to derive the tuning parameter for the tuned pseudoatom automatically.

Specific Initiatives

Multiscale approaches for the treatment of explicit local solvation environments with embedding to include longer-range solvent effects



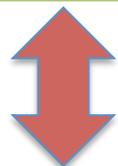
Challenge: Strong interactions (e.g., hydrogen-bonding) cause preferential solvation and require explicit local solvation environments; other examples of non-uniform solvent environments include highly compressible fluids (e.g., supercritical CO₂) and interfaces.

Plan: Develop a Monte Carlo procedure for the efficient generation of minimal sets of representative explicit solvent configurations (MC-MSREX) and additional embedding in a polarizable continuum model

Representative Sub-task

Multiscale approaches for the treatment of explicit local solvation environments with embedding to include longer-range solvent effects

Automatic generation of a large number of uncorrelated explicit solvent configurations using MD/MC with KS-DFT or MM description
Development of a fitness function to measure whether a subset of these configurations is representative of the entire ensemble
MC simulated annealing/genetic evolution algorithm for pruning of subsets



NWChem program
Computation of ground- and excited-state wave functions and convergence control

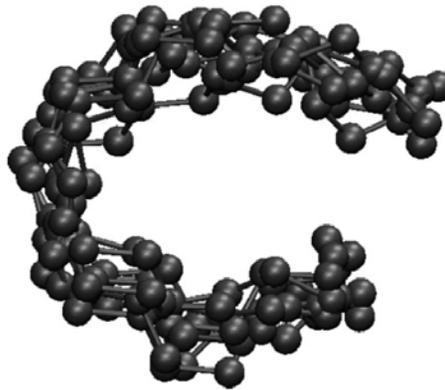
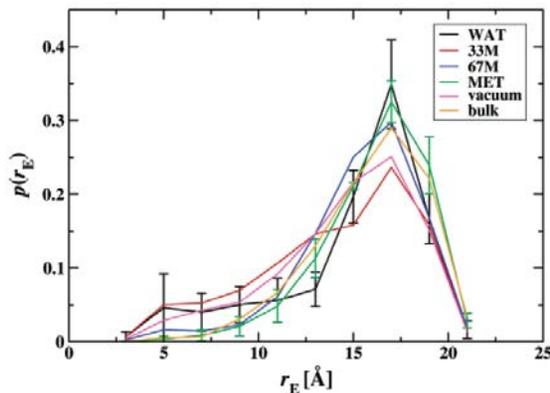
Mathematical issue: Provide mathematical definition of fitness function

Scientific issue: Can pruned subset describe ensemble of solvent configurations?

Algorithmic issue: What is the most efficient way to prune and to check for convergence?

Specific Initiatives

Monte Carlo strategies for efficient conformational sampling of large and flexible chromophores



Challenge: Flexible chromophores can access multiple conformational states with the distribution influenced by solvation effects; conformational states are often separated by large free energy barriers requiring specialized sampling approaches.

Left: Distribution of end-to-end distances for *n*-octadecane in various environments (water, 33/67 MeOH/H₂O, 67/33 MeOH/H₂O, methanol, gas phase, bulk C18)

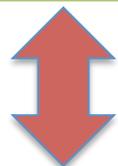
Right: Overlay of *uncorrelated* folded conformations of hydrated C18 chains

Plan: Develop a Monte Carlo procedure for the efficient generation of minimal sets or representative chromophore conformations (MC-MSCON) and solvent configurations

Representative Sub-task

Monte Carlo strategies for efficient conformational sampling of large and flexible chromophores

Automatic generation of a large number of uncorrelated chromophore conformations using configurational-bias Monte Carlo approaches
Development of a fitness function to measure whether a subset of these conformations is representative of the entire ensemble
MC simulated annealing/genetic evolution algorithm for pruning of subsets



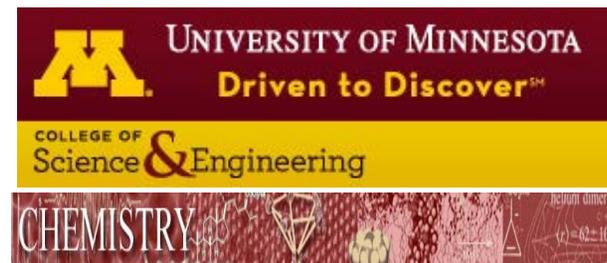
NWChem program
Computation of ground- and excited-state wave functions and convergence control

Mathematical issue: Provide mathematical definition of fitness function

Scientific issue: Can pruned subset describe ensemble of chromophore conformations?

Algorithmic issue: What is the most efficient way to prune and to check for convergence?

The Logo that Dare not Speak Its Name



Challenges Associated with the Development of Electron-Correlated Methods for Excited State Structure and Dynamics

See also poster presentation by

Laura Gagliardi

SciDAC Kickoff Meeting, September 2012

