SciDAC Scientific Computation Application Partnership

University of Minnesota

Pacific Northwest National Laboratory

Lawrence Berkeley National Laboratory

Charge Transfer and Charge Transport in Photoactivated Systems

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

A suite of new theoretical methods will be *developed* and *implemented* in the *NWChem* computational chemistry software suite in order to provide *improved* capabilities for excited-state dynamics in the gas phase and to *add* the capability to perform electronically excited-state dynamics in solution. Successful implementation will be transformative for the study of photochemical reactions with levels of accuracy similar to those commonly available for ground-state thermal reactions. Developed methods will have a broad impact as they will be implemented in a robust, widely available, actively supported software environment. The implementation will benefit from the expertise of the *NWChem* development team and infrastructure at the Environmental Molecular Science Laboratory and from dedicated "guinea pig" end users. It will also benefit from the expertise of people at the SciDAC Institute for Frameworks, Algorithms, and Scalable Technologies for Mathematics (FASTMATH) and at the SciDAC Institute for Sustained Performance, Energy, and Resilience (SUPER).

This SciDAC partnership will synergistically develop and implement problem-driven, efficient and scalable electronic structure methods including:

I) Theory and code to perform calculations with variations on complete-active-space (CAS) type wave functions including generalized-active-space (GAS) and split-CAS wave functions. Second-order perturbation theory will also be implemented for these wave functions. Relativistic effects will be included for all-electron calculations.
II) Theory and code to compute state-specific non-equilibrium and equilibrium continuum solvation effects for molecular excited-states.
III) Algorithms and codes for the treatment of electronically nonadiabatic dynamics in both the gas-phase and solution. These models will permit the study of (i) time-dependent fluorescence, (ii) other early-time photophysical processes, and (iii) general photochemistry (the use of photons to induce chemical reactions). Modified fewest-switches time-uncertainty (FSTU) and coherent switches with decay of mixing (CSDM) semiclassical algorithms will be implemented to function with the molecular dynamics package of the *NWChem* program.
IV) Theory and code to interpolate diabatic surfaces for photochemical reactions taking place in the condensed phase using the electrostatically embedded multiconfiguration molecular mechanics and molecular mechanics (EE-MCMM/MM) scheme. The combination of the above methods for diabatization, efficient multireference calculations, and the EE-MCMM/MM scheme for quantum-mechanical/molecular-mechanical (QM/MM) calculations will make

possible the modeling of large and complex systems beyond the reach of current protocols.

V) Theory and code to enable the atomistic treatment of explicit *local* solvation environments but further embedded within a polarized continuum model to include longer-range solvent effects. Methods will be developed to identify small but representative subsets of solvent configurations for mixtures (including ionic liquids), compressible fluids, and interfaces.

VI) Theory and code to enable efficient conformational sampling for chromophores based on configurational-bias Monte Carlo strategies. For very large flexible chromophores (e.g., polymeric dyes), simulated annealing schemes will be optimized to generate subsets of most representative conformations.

Math challenges include the solution of large dimensional generalized nonsymmetric eigenvalue problems associated with GASSCF and Split-CAS models. Our intent is to explore a variety of methods, including *PARPACK*, *Jacobi-Davidson*, and subspace iteration. Another key challenge will be the development and implementation of efficient schemes for propagating trajectories and sampling phase space in very-high-dimensional multiscale simulations including quantum mechanical and classical mechanical representations of molecular and electronic degrees of freedom.

Computer science challenges include ensuring that new algorithmic implementations are developed with parallelism embedded in the governing equations so as to map them onto the Global Array Toolkit framework in *NWChem* in a fashion that ensures that they will scale up to thousands of cores upon insertion in the code. We will also investigate the use of OpenMP threading with suitable memory mapping under the Global Array Toolkit to better address multicore architectures, and we will leverage ongoing developments to accelerate calculations where general purpose GPU computing may prove helpful. Efficient management of input and output (I/O) during computations will also be an essential factor for keeping the computing framework scalable. We will leverage a variety of performance analysis tools being developed collaboratively via the SUPER institute including IPM, TAU, and HPCToolkit to identify and characterize performance workload. We will then delve into performance optimization of the bottlenecks at both the algorithmic and implementation levels to develop efficient mapping of the computational components to multicore, many-core, and heterogeneous architectures.

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