

Quantum-Classical Path Integral Simulation of Charge Transfer Reactions

PI: Nancy Makri, University of Illinois at Urbana-Champaign

Co-PI(s): Peter L. Walters, University of Illinois at Urbana-Champaign

Corresponding author: Nancy Makri, nmakri@illinois.edu

Executive Summary

Quantum mechanical calculations on condensed phase or biological systems are prohibitively expensive. Mixed quantum-classical approximations are highly efficient and attractive. However, conventional quantum-classical methods introduce major assumptions in the treatment of the interaction between quantum and classical degrees of freedom. We have developed a rigorous quantum-classical path integral (QCPI) methodology which is free of assumptions and which treats all interactions in full atomistic detail. Our QCPI simulation on Blue Waters of the ultrafast ferrocene-ferrocenium electron transfer reaction in liquid hexane yielded results of unprecedented accuracy and enabled the first quantitative demonstration of Gaussian behavior for a complex molecular solvent. Additional theoretical and algorithmic advances enabled simulation of reactions that span very different time scales. In particular, simulation of this process in a series of solvents with increasing polarity exemplified the interplay between electronic/molecular time scales and energetics and its effects on the kinetics of charge transfer reactions.

Key Challenges

Tunneling, quantum dispersion and phase interference play a subtle but very important role in many chemical and biological processes. Quantum mechanical simulations of dynamical processes in the condensed phase continue to be extremely challenging because quantum mechanics is a non-local theory, implying an exponentially growing cost with the number of interacting particles.

For many processes of interest, quantum mechanical effects are essential only in the treatment of a small number of particles (e.g., a proton, or a small number of electronic states associated with a charge transfer reaction). The remaining particles (solvent molecules or biological medium) can be adequately described via classical dynamics. Unfortunately, the traditional Schrödinger formulation of quantum mechanics (which is based on delocalized wave functions) is incompatible with Newtonian trajectories (which are local in space). Within this formulation, the interaction between the quantum and classical partitions cannot be treated without resorting to severe approximations.

Why it Matters

To address the major challenges encountered in the simulation of such processes, our group has developed a rigorous quantum-classical formulation based on Feynman's path integral formulation of quantum mechanics. The local nature of the Feynman paths leads naturally to quantum-classical treatments that are free of *ad hoc* assumptions. The quantum-classical path

integral (QCPI) methodology that we developed is a rigorous quantum-classical formulation. However, the QCPI expression appears impractical, as it contains an astronomical number of terms. Several advances in the understanding of interference and decoherence have recently made the QCPI methodology practical for the simulation of condensed phase reactive processes.

QCPI treats the small system of interest by full quantum mechanics, while the effects of the environment are captured via standard molecular dynamics (MD) procedures. Two widely used MD packages, NAMD and LAMMPS, are used to yield trajectories subject to forces obtained using the coordinates of the charged particle, which are specified by the given path. The dynamics captured along a classical trajectory augments the Hamiltonian of the quantum system through a time-dependent term, which leads to level fluctuations and eventually to decoherence. The exponential proliferation of trajectories with propagation time is avoided through a tensor decomposition that exploits the memory-quenching effects of condensed phase environments. The QCPI algorithm is characterized by classical molecular dynamics scaling and is fully parallelizable.

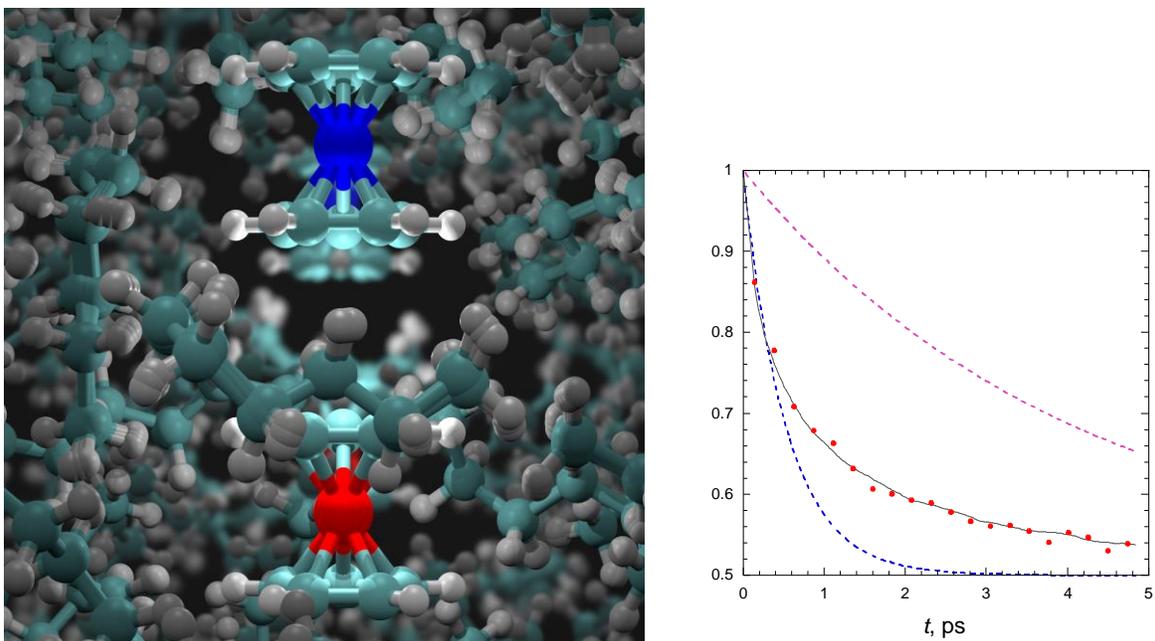


Fig. 1. Left panel: A close-up snapshot of the ferrocene-ferrocenium charge transfer simulation in liquid hexane, showing the solvent configurations arising from the superposition of three quantum-classical paths. C and H atoms are shown in cyan and white. The Fe^{2+} and Fe^{3+} ions are shown in blue and red, respectively. Right panel: Comparison of converged all-atom results for the donor population (red markers) against those obtained with the harmonic bath model (black line). Also shown are exponential decay curves with the rate coefficient extracted from the long-time exponential behavior of the population (dashed violet line) and the Marcus expression (dashed blue line), respectively.

Why Blue Waters?

The QCPI formulation is well suited to a decomposition based on multi-level parallelism, and Blue Waters provides the ideal platform for its implementation. Specifically, the set of system paths is distributed across nodes; one processor within each node is assigned to the quantum mechanical calculations, while the other performs supporting trajectory computations. Moreover, because the trajectories are independent and generally relatively short, it is possible to assign a single trajectory to each core within a given processor while maintaining computational efficiency. This multi-level approach has the benefit of minimizing communication time while maximizing concurrent processing.

Accomplishments

The QCPI methodology has enabled the simulation of charge transfer reactions in solution with unprecedented accuracy. The dynamics of the prototypical ferrocene-ferrocenium electron transfer pair was studied in a series of organic solvents of increasing polarity. Our first simulation of this electron transfer reaction in liquid hexane employed 1320 atoms interacting via CHARMM force fields. More recent work has studied the same reaction in a series of solvents of increasing polarity.

The all-atom QCPI simulations shed light on the complex interplay between molecular/solvent time scales, electronic couplings and reorganization energy, in particular on the way that these effects determine the rate of the reaction, the nature (exponential or nonexponential) of the dynamics, and the validity of Gaussian response. They also demonstrate how the interference among quantum mechanical phases leads to decoherence, and reveal substantial quantum delocalization of the otherwise classical solvent as a result of its interaction with the quantum electron transfer pair.

Publications and Data Sets

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Makri, N., Interference, Decoherence, and Quantum-Classical Path Integral Simulations with Thousands of Atoms, American Conference on Theoretical Chemistry, Boston University, July 2017.

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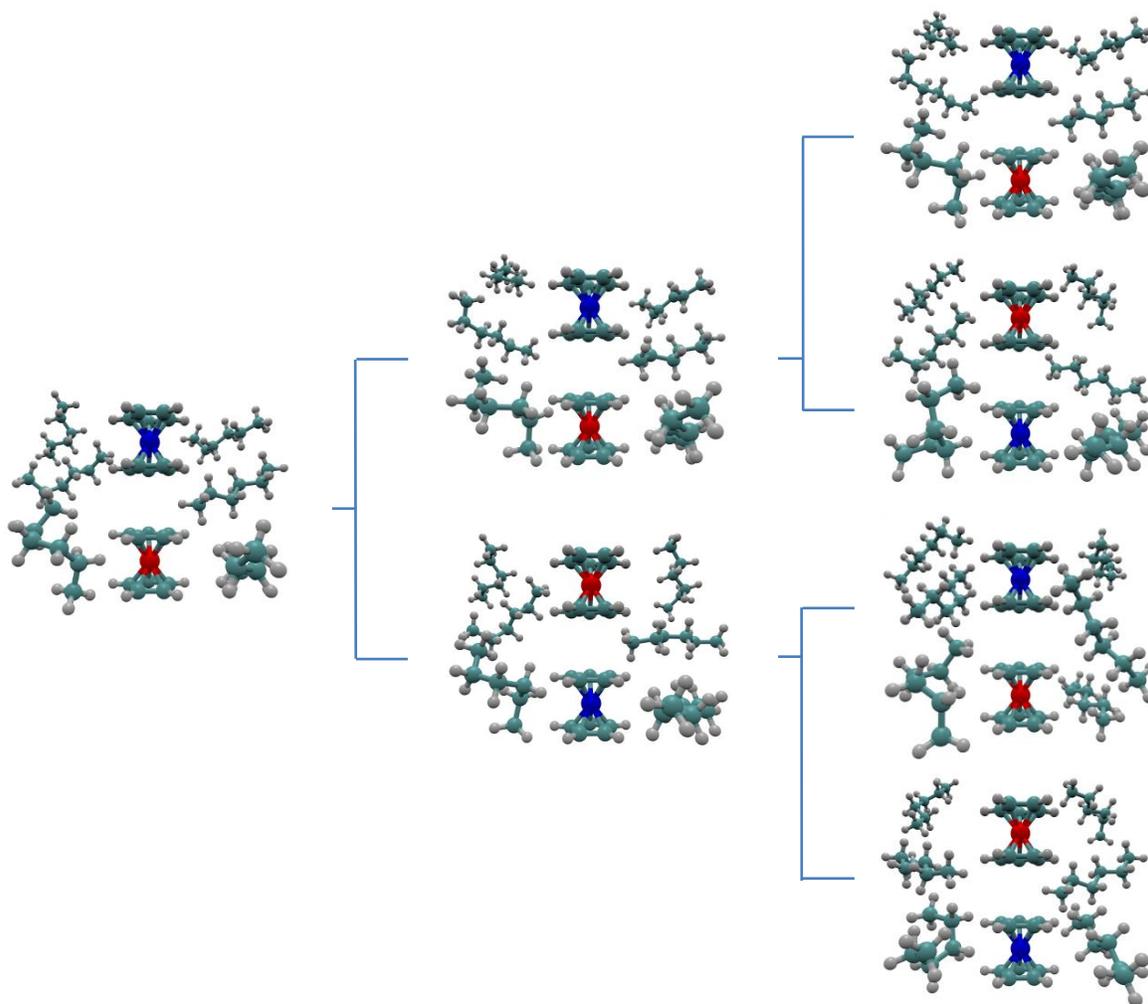


Fig. 2. Solvent trajectories during the first two time steps of the ferrocene-ferrocenium electron transfer simulation. Blue and red correspond to the reduced and oxidized iron atoms. The solvent molecules surrounding the ferrocene-ferrocenium complex are seen to respond to the change of electronic configuration.