



QUANTUM-CLASSICAL PATH INTEGRAL SIMULATION OF CHARGE TRANSFER REACTIONS

FIGURE 1: A snapshot of the simulation after approximately 0.4 ps showing the solvent configuration arising from the superposition of three quantum-classical paths.

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EXECUTIVE SUMMARY

Quantum mechanical effects play an essential role in chemical and biological processes. However, it is impossible, as well as unnecessary, to treat every particle involved in these processes quantum mechanically. Our group has recently developed a rigorous quantum-classical path integral (QCPI) methodology [1-4] in which a few of the particles are treated by full quantum mechanics, and the effects of the remaining particles are captured via classical trajectories. The QCPI approach is free of *ad hoc* assumptions, allowing a faithful description of the interaction between the quantum and classical particles. Its implementation on Blue Waters provides a detailed picture of charge transfer in solution with **unprecedented** accuracy.

INTRODUCTION

Quantum mechanical effects are prominent in many chemical and biological processes, yet they present a major challenge to simulation. Quantum mechanics is non-local in nature, which leads to an exponential scaling of the computational cost with the number of interacting particles. Thus, the computational

effort required for simulating these processes, which contain many thousands of particles, with quantum mechanics is astronomically large.

For many processes of interest, quantum mechanical effects are only vital in the treatment of a small number of particles (e.g., those corresponding to a transferring charge). The remaining particles (solvent molecules or biological medium) can be adequately described via Newtonian dynamics. While this partitioning makes the simulations computationally feasible, the interaction between the classical and quantum partitions must be treated with care. The traditional Schrödinger formulation of quantum mechanics (which is based on delocalized wave functions) is incompatible with Newtonian trajectories (which are local in space). In the Schrödinger formulation, the interaction between the quantum and classical partitions cannot be obtained without introducing severe approximations.

METHODS & RESULTS

The Makri group's aim has been the development of rigorous quantum-classical formulations

based on Feynman's path integral formulation of quantum mechanics [5]. The trajectory-like nature of the Feynman paths leads naturally to combined quantum-classical treatments. Unlike wave functions, Feynman paths are local in space. Thus these combined treatments are free of approximations. Recent work has described a QCPI methodology, which incorporates these ideas as well as several advances in the understanding of decoherence (loss of coherence) processes [6]. QCPI treats a small subsystem 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 current project involves the **first** implementation of QCPI to the simulation of charge transfer in condensed media, which is a key feature of many chemical and biological processes. Using traditional quantum methods to simulate the dynamics accurately in such cases is practically impossible. However, with QCPI, these simulations become feasible. Our recent work has focused on two prototypical charge transfer reactions. The first involves the transfer of an electron between the ferrocene-ferrocenium charge transfer pair in solution (hexane, hexene and various mixtures of the two). The second is the proton transfer reaction for the phenol-amine complex in methyl chloride [7]. We have accurately simulated the dynamics of the charge transfer and obtained the time evolution of the state populations for the ferrocene-ferrocenium pair in hexane, and for the phenol-amine complex in methyl chloride. These were carried out at the full atomistic level and represented the **first** of their kind.

Additionally, we performed the same simulations with the solvent replaced by an effective bath of harmonic oscillators. This was done to help quantify the validity of linear response for such systems [8].

The QCPI simulations shed light on the complex interplay between the classical solvent and the quantum system at an atomistic level. Figure 1 shows the delocalizing effect that the quantum electron transfer has on the classical hexane solvent. It is apparent that even for solvents that are weakly coupled to the charge transfer, such as hexane, the system's influence on the solvent cannot be ignored.

Upon completion of the present phase of this work, we will obtain quantitative results for the dynamics of the ferrocene-ferrocenium charge transfer in

hexene and in hexane-hexene mixtures. This will allow for a greater understanding of how stronger system-solvent coupling impacts the dynamics of electron transfer in solution. Additionally, we will be able to further test the validity of linear response in these less hospitable regimes.

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 since related classical and quantum-mechanical calculations are performed within the same node, where inter-processor communication should be much faster than if the information were more widely distributed.

NEXT GENERATION WORK

With the power of next generation of supercomputers it should be possible to use QCPI to accurately simulate the dynamics of complex charge transfer reactions containing multiple quantum particles and possessing long lived quantum coherence.

PUBLICATIONS AND DATA SETS

Walters, P. L., and N. Makri, Quantum-classical path integral simulations of ferrocene-ferrocenium charge transfer in liquid hexane. *J. Phys. Chem. Lett.*, 6 (2015), 4959–4965, doi:10.1021/acs.jpcllett.5b02265

Walters, P. L., and N. Makri, Quantum-classical path integral simulations of ferrocene-ferrocenium charge transfer in solution. *251th ACS National Meeting & Exposition*, San Diego, Calif., March 13-17, 2016.