Quantum-classical path integral simulation of proton transfer in solution

Executive Summary:
Quantum mechanical effects play an essential role in chemical and biological processes. Our group has recently developed a rigorous quantum-classical path integral (QCPI) methodology that incorporates these ideas as well as several advances in the understanding of decoherence (loss of coherence) processes. QCPI treats a small subsystem by full quantum mechanics, while the effects of the environment are captured via classical trajectories. The QCPI approach is free of ad hoc assumptions, allowing a faithful description of interference effects and leading to correct product distributions. Its implementation on Blue Waters provides a detailed picture of proton 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. The main difficulty in the development of quantum mechanical simulation algorithms stems from the non-local nature of quantum mechanics, which leads to exponential scaling of computational effort with the number of interacting particles. For many processes of interest, quantum mechanical effects are vital in the treatment of a small number of degrees of freedom (e.g., those corresponding to a transferring proton), while the remaining particles (solvent molecules or biological medium) could be adequately described via Newtonian dynamics. However, the traditional Schrödinger formulation of quantum mechanics (which is based on localized wave functions) does not lend itself to a combination with Newtonian trajectories (which are local in phase space) unless severe approximations are introduced.

Methods & Results:
The Makri group has been pursuing rigorous quantum-classical formulations based on Feynman’s path integral formulation of quantum mechanics. The major appeal of this approach stems from the local, trajectory-like nature of the Feynman paths, which leads naturally to combined quantum-classical treatments that are free of approximations. Recent work has described a quantum-classical path integral (QCPI) methodology, which incorporates these ideas as well as several advances in the understanding of decoherence (loss of coherence) processes. QCPI treats a small subsystem by full quantum mechanics, while the effects of the environment are captured via standard molecular dynamics (MD) procedures. Since all quantum interference effects and their quenching by the solvent are accounted for at the most detailed (non-averaged) level, QCPI leads to correct branching ratios and product distributions, allowing simulations of important chemical and biological processes with unprecedented accuracy.

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The present project involves the first implementation of QCPI to the simulation of the proton transfer reaction for the phenol-amine complex in methyl chloride. This system is considered a paradigm for proton transfer and has served as a model for many computational investigations using a variety of approximations. Accurate QCPI calculations are being performed at the full atomic level, as well as within the linear response approximation, in which the solvent is replaced by an effective bath of harmonic oscillators. Thus, the results will also help quantify the validity of linear response on a realistic proton transfer system.