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New insights into the nonadiabatic dynamics of proton-coupled electron transfer reactions from the mixed quantum-classical Liouville approach GABRIEL HANNA, FARNAZ SHAKIB, University of Alberta — The nonadiabatic dynamics of model proton-coupled electron transfer (PCET) reactions is studied for the first time using a surface-hopping solution of the mixed quantum-classical Liouville (MQCL) equation. In contrast to Fewest Switches Surface-Hopping (FSSH), which is commonly used in the simulation of PCET, the MQCL approach provides a rigorous treatment of decoherence in dynamics simulations of MQC systems. The studied model consists of a proton and an electron in a donor-acceptor complex (i.e. quantum subsystem) and a collective solvent coordinate (i.e. classical environment). Using this model, both concerted and sequential PCETs are studied under different proton/electron-solvent coupling conditions, and insights into the dynamical principles underlying these reactions are gained. Notably, an analysis of the trajectories reveals that the solvent coordinate spends a large fraction of its time on the mean of two coherently coupled potential energy surfaces (PESs), as opposed to on single PESs as in the FSSH approach. The results of this study not only demonstrate the applicability of the MQCL approach for PCET simulations, but also emphasize the importance of incorporating decoherence effects through mean surface evolution into calculations of PCET rate constants.

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