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Model path-integral dynamics for nonadiabatic reactions in the condensed phase NANDINI ANANTH, Cornell University, ARTUR MENZELEEV, THOMAS MILLER, California Institute of Technology — We introduce mapping-variable ring polymer molecular dynamics (MV-RPMD), a direct, real-time dynamic technique for the atomistic simulation of nonadiabatic reactions. The dynamics are based on the recently derived exact path-integral Stock-Thoss (PI-ST)representation for the quantum Boltzmann operator that has been previously used to calculate equilibrium properties for N-level systems, and as a way to initialize semiclassical trajectories for the calculation of thermal correlation functions. Both these methods use the Stock-Thoss (ST) mapping protocol to map from a discrete electronic states basis to a continuous Cartesian variables basis, providing the even-handed treatment of electrons and nuclei required to accurately describe their dynamically coupled motions and to describe resonance energy transfer. Like the existing RPMD approach, this method can be used to generate statistically meaningful ensembles of reactive trajectories but, unlike RPMD, it is applicable to photochemical reactions and reactions where proper electronic state quantization is essential. We present the results of simulations using MV-RPMD to calculate correlation functions for a series of model N-level systems over a wide range of nonadiabatic coupling strengths.

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