Long-time description of zero-point energy in high-dimensional molecular systems using the approximate quantum trajectories

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Abstract

Reactions in complex molecular systems often unfold on a picosecond timescale. To accurately simulate such dynamics we further develop the approximate quantum trajectory formalism [1] to give stable long-time description of zero-point energy effect in anharmonic systems of high dimensionality [2]. The method is based on a numerically cheap linearized quantum force; stabilizing terms compensating for the linearization errors are added into the time evolution equations for the classical and nonclassical components of the momentum operator. The wavefunction normalization and energy are rigorously conserved. The method is exact for correlated Gaussian wavepackets in locally harmonic potentials, and it describes the localization energy for moderately anharmonic systems for hundreds of oscillation periods. Numerical tests are performed for model systems of up to 40 degrees of freedom. The approach is suitable to model proton transfer coupled to a high-dimensional anharmonic bath.

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[1] S. Garashchuk and V. A. Rassolov. Energy conserving approximations to the quantum potential: Dynamics with linearized quantum force. *J. Chem. Phys.*, 120:1181–1190, 2004.

[2] S. Garashchuk and V. A. Rassolov. Stable long-time semiclassical description of zero-point energy in high-dimensional molecular systems. *J. Chem. Phys.*, 129:024109, 2008.