Semiclassical investigation of nuclear quantum effects in chemical kinetics and vibrational spectroscopy

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Abstract
Nuclear Quantum Effects (NQE) manifest in chemistry in both kinetics and spectroscopy fields. Accounting for the Zero Point Energy (ZPE) and tunneling phenomena can explain unexpected experimental observations of reaction rate constants.[1,2] Also, in spectroscopy, some spectral features, such as signal splittings or shifts, are due to tunneling phenomena or quantum delocalization (or localization), which cause the system to sample the potential energy surface in a non-classical way.[3,4] Rigorous but at the same time, affordable methods to include NQE in atomistic simulations must be developed to predict and explain experimental quantum mechanical hallmarks. This talk will describe semiclassical approaches for kinetics and spectroscopic applications. Specifically, the Semiclassical Transition State Theory (SCTST) can include tunneling and ZPE effects at a higher level of theory than widespread tunneling corrections for classical TST rate calculations.[5-7] Then, the Semiclassical Initial Value Representation Molecular Dynamics (SC-IVR-MD) can predict accurate vibrational spectra and even reproduce vibrational quantum eigenfunctions.[9,10] Thus, the SC-IVR-MD technique can reproduce the quantum mechanical sampling of the potential energy surface, fixing purely classical MD vibrational spectroscopy pitfalls.[11]

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