

Toward Ab Initio Molecular Dynamics on Many Electronic States

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Ab initio molecular dynamics methods enable the simulation of chemical reactions without prior knowledge of the potential energy surface or reaction coordinate. Many methods exist for modeling dynamics on the ground electronic state or on a few low-lying excited electronic states, but most of these become impractical for systems with dense manifolds of electronic states, such as those that arise upon high energy excitation. Ehrenfest molecular dynamics, on the other hand, does not require explicit knowledge of the electronic eigenspectrum, and therefore is a practical tool for modeling dynamics on many states. However, Ehrenfest suffers from well-known issues with overcoherence. We propose novel variants of Ehrenfest molecular dynamics that incorporates decoherence. These methods are based on the recognition that the history of the electronic wave function can be used to compute approximate eigenstates, so that the full eigenspectrum of the electronic Hamiltonian need not be computed. We will demonstrate the accuracy of this method by application to several model potentials. To provide on-the-fly electronic structure calculations for our simulations, we have developed graphics processing unit accelerated time-dependent complete active space configuration interaction (TD-CASCI) and multireference configuration interaction singles (TDMRCIS) tools. Akin to time-independent direct configuration interaction methods, our algorithm does not require formation or storage of any data structures with the full dimension of the Hamiltonian, enabling the use of large configuration spaces. These tools have been applied to predict electronic dynamics in large, strongly correlated molecules (up to decacene; $C_{42}H_{24}$). Finally, we will demonstrate the incorporation of an explicit light field via an efficient implementation of Floquet configuration interaction (F-CI). The Floquet (dressed state) approach naturally incorporates decoherence effects related to the photon state of the system. Again, our implementation draws inspiration from time-independent direct configuration interaction methods to avoid the formation of large data structures. Together, these developments represent important steps toward a general tool for accurately and efficiently modeling nonadiabatic molecular dynamics on many electronic states.