Correlated Electron-Nuclear Dynamics for Extended Systems Based on Exact Factorization

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Correlated electron-nuclear dynamics is crucial in various phenomena, including photosynthesis, photovoltaics, photocatalysis, radiation chemistry, polaron chemistry, and quantum computing. Electron-nuclear correlations are handled using mixed quantum-classical approaches for small and intermediate molecular systems.[1] However, for extended molecular systems, real-time time-dependent density functional theory (RT-TDDFT) is used frequently. RT-TDDFT propagates electronic density with time-dependent Kohn-Sham orbitals and time-dependent external potentials while the classical nuclei move according to the Ehrenfest-type equation of motion. While the electronic equation of motion can describe nonadiabatic transitions, it cannot account for nuclear wave packet splitting and quantum decoherence, which are crucial for describing long-time behavior. To overcome this limitation, we propose a Hermitian form of an electron-nuclear correlation operator, which is equivalent to the original non-Hermitian operator.[2] This approach obtains a stable real-time and real-space electronic propagation with quantum decoherence in correlated electron-nuclear dynamics, which is essential for condensed phase simulations. Furthermore, we devise a modified version of the time-dependent Kohn-Sham equation by employing a Hermitian correlation operator within the RT-TDDFT framework. The approach is demonstrated to work well for molecular and condensed matter systems. The proposed method may pave the way for using the RT-TDDFT framework with the electron-nuclear correlation from the exact factorization approach for the simulation of extended systems for material science applications where a large number of electronic Born-Oppenheimer states are involved in the dynamics.

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