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Long Time Behavior of Time-Dependent Density Functional Theory

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In principle, Time-Dependent Density Functional Theory (TDDFT) could be used to calculate the thermodynamic properties of systems of electrons using an approach that is analogous to the way in which classical molecular dynamics (MD) is used to calculate the properties of systems of atoms. The development of such an approach requires an understanding of long-time behavior and equilibration in TDDFT. For a variety of systems (e.g., many metals), experiments suggest that the electronic subsystem reaches an effective state of internal equilibrium due to electron-electron scattering on a time scale that is short compared to electron-phonon equilibration. Consider a TDDFT simulation in which such a system starts from the ground state, is excited by a time-dependent potential, and then is allowed to evolve after the time-dependent potential has been turning off. To the extent that internal equilibration of the electrons creates changes in the electronic density, exact TDDFT should be able to capture the equilibration process in such a system. We investigate the extent to which practical TDDFT calculations can also capture this behavior by performing long-time (multi-picosecond) TDDFT simulations of aluminum using the adiabatic local-density approximation (LDA). We monitor the equilibration process by calculating the projections of the TDDFT states into the Kohn-Sham eigenvectors of the system and averaging these projections within time windows. For a system of non-interacting Fermions at equilibrium, the ensemble average of these projections would follow a Fermi distribution, but for interacting systems (e.g., a Fermi liquid), the resulting distribution can be modified. Using a recently published algorithm (Modine and Hatcher, JCP 142, 204111 (2014)), we construct initial TDDFT states whose average projections match a Fermi distribution. During TDDFT propagation of these states, the calculated projections are observed to evolve away from the Fermi distribution to a modified distribution with a sharper drop at the Fermi level and longer tails at high and low energies.

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