Representing the Thermal State in Time-Dependent Density Functional Theory

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Classical molecular dynamics (MD) provides a widely used approach to determining thermodynamic properties by integrating the classical equations of motion of a system of atoms. Time-Dependent Density Functional Theory (TDDFT) provides a powerful approach to integrating the quantum equations of motion of a system of electrons. In analogy to MD, one could imagine obtaining the thermodynamic properties of an electronic system from a TDDFT simulation. For a variety of systems (e.g., many metals), the electronic subsystem reaches an effective state of internal equilibrium on a time scale that is short compared to electron-phonon equilibration. During the initial time-evolution of such systems, electron-phonon interactions should be negligible, and therefore, TDDFT should be able to capture the thermalization of the electronic subsystem. However, it is unclear how TDDFT represents the resulting thermal state. The thermal state is usually represented in quantum statistical mechanics as a mixed state, while TDDFT simulates the unitary evolution of a many-electron pure state, which is mapped by the TDDFT formalism into a fictitious non-interacting system. We work to address this puzzle by: (A) Reformulating quantum statistical mechanics to evaluate thermodynamic expectations as an unweighted average over a set of many-body pure states, and (B) Constructing a family of non-interacting (single determinant) states that approximate the required many-body states.

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.