Comparison of Density Functional Approximations and the Finite-Temperature Hartree-Fock Approximation: Warm Dense Lithium

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Extreme chemistry (long-lived transient molecular species, multiple ionic species, etc., all at electron temperatures of several eV) characterizes warm dense matter (WDM). Current WDM simulations use molecular dynamics for the ions driven by finite-temperature Density Functional Theory (ftDFT) forces computed using ground state approximate functionals (mostly), in either Kohn-Sham form or in orbital-free form using Thomas-Fermi and similar approximations. Thus there is pressing need both for better functionals and for understanding the behavior and limitations of the use of ground state functionals.

This study probes the behavior of ftDFT using both ground-state and temperature-dependent approximate functionals by comparison with the finite-temperature Hartree-Fock (ftHF) approximation. The prototype WDM system is bcc Li in the appropriate temperature-density regime. For exchange only, we find major qualitative differences between exact ftHF and ftDFT with the zero-temperature local density approximation (LDA) functional. A temperature-dependent LDA gives much better agreement.

Reliable pseudopotentials for the WDM regime are an essential technical ingredient for such calculations. We have tested pseudopotentials by comparison with all-electron results for small Li clusters of local bcc symmetry and bond-lengths appropriate to WDM bulk Li. This allows determination of the density range over which standard projector-augmented wave (PAW) data sets and norm-conserving pseudopotentials are reliable. We also present new, small-cutoff-radius PAW sets (for both the LDA and the generalized gradient exchange-correlation approximations) which are valid for lithium densities up to at least 80 g/cm^3.

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