

Basis set convergence for first-principle electronic free energy calculations

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We investigated the basis set size (M) dependence for finite temperature quantities in the canonical ensemble using the exact fit-FCI method. Studies are conducted for the uniform electron gas (UEG) and helium using a plane-wave basis, and this is contrasted with an isolated hydrogen atom. Several of the convergence behaviors are related to the momentum distribution ($n(q)$) and static structure factor ($S(q)$). In the canonical ensemble for $T > 0$, the free energy can be a variational quantity with M , rather than U . We find that the free-energy convergence for warm to low T matches the known $U(T=0)$ convergence rates of M^{-1} for unpolarized and $M^{-5/3}$ for fully polarized systems.

Research was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences Early Career Research Program (ECRP) under Award Number DESC0021317. Computer resources for this project were also provided from the University of Iowa.