Temperature-dependent Green's functions for the electron-correlation problem in extended systems

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Abstract

The inclusion of temperature in the electronic-structure calculations appears essential in systems with small band gaps providing for non-negligible occupancies of the excited states even at ambient temperatures. Green's function methods offer a powerful tool for solving the electron-correlation problem, competitive with traditional quantum chemistry approaches. Among advantages of the former, there is a built-in accounting for temperature via the Matsubara formalism. The resulting temperature-dependent Green's function is directly related to the thermodynamic properties of a system via the grand potential.

We have implemented a temperature-dependent self-consistent perturbative second-order Green's function method (GF2) for periodic systems with the full realistic Hamiltonian. Though it is the lowest-order non-trivial approximation for electronic correlations, it proves capable of revealing a variety of regimes even in a deceptively simple system, one-dimensional periodic hydrogen, showing emergence of metallic, band insulator, and Mott insulator phases.

As a non-linear procedure, GF2 can converge to different solutions depending on the initial guess. At a finite temperature, the GF2 total energy corresponding to the thermodynamic internal energy is insufficient to determine the most stable phase. Including the entropic contribution derived from the grand potential and comparing the Helmholtz energies is instrumental in discerning the phases and determining phase stability at a given temperature. We show that all these thermodynamic quantities can be obtained from the self-consistent second-order Green's function theory.