

Thermodynamics from a Second Order Green's Function Method

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Green's functions methods are alternative to wave function and density based methods in electronic structure theory. Within these methods, it is possible to include the temperature dependence explicitly without any additional implementation. In this work, we use a temperature dependent second order Green's function method (GF2) to evaluate the grand potential from the functional of Luttinger and Ward. The grand potential gives us access to the electronic partition function, and can in principle calculate any quantity that can be obtained from it. To demonstrate our method, we have evaluated quantities such as Helmholtz energy and entropy for molecules in a small basis, and are able to obtain excellent agreement with temperature dependent full configuration interaction (FCI) calculations at a high temperature. We additionally calculate entropy for periodic hydrogen chains at various temperatures and in doing so are able to determine the relative stability of each phase.