

Thermodynamics as a Foundation for Density Functional Theory

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Density Functional Theory (DFT) is the method of choice for an ever increasing number of electronic structure computations (recently reaching 30,000 publications per year). It was founded in the sixties on the basis of the Hohenberg-Kohn theorem and the Kohn-Sham equations, which were originally proved and derived for electronic ground states. Alternatively, one may use thermodynamics to derive DFT for finite-temperature ensembles, with the ground-state theory recovered in the zero temperature limit. Specifically, the transformation from chemical potential μ to electron number N as a free variable may be directly generalized to clarify how DFT uses the density distribution $n(\mathbf{r})$, rather than the external potential $v(\mathbf{r})$, to specify a particular inhomogeneous electronic system. Relating interacting and non-interacting systems with the same $n(\mathbf{r})$ distribution, one recovers not only the Kohn-Sham formulation, but also the so-called adiabatic connection theorem, which gives an explicit expression for the exchange-correlation energy in terms of the "exchange-correlation hole." This derivation has the advantage of being constructive, rather than being based on a *reductio ad absurdum* argument. It thus serves as an excellent basis for a discussion of the approximations which are inevitably introduced, including the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA).

Reference:

[1] N. Argaman and G. Makov, "Density Functional Theory – an Introduction," *Am. J. Phys.* **68**, 69 (2000).