



Basic rules for functional construction at finite temperature

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Because of the small mass ratio between electrons and nuclei, standard electronic structure calculations treat the former as being in their ground state, but routinely account for the finite temperature of the latter, as in *ab initio* molecular dynamics [1]. But as electronic structure methods are applied in ever more esoteric areas, the need to account for the finite temperature of electrons increases. Phenomena where such effects play a role include rapid heating of solids via strong laser fields [2], dynamo effects in giant planets [3], magnetic [4] and superconducting phase transitions [5, 6], shock waves [7], warm dense matter [8], and hot plasmas [9].

Within density functional theory, the natural framework for treating such effects was created by Mermin [10]. Application of that work to the Kohn-Sham (KS) scheme at finite temperature also yields a natural approximation: treat KS electrons at finite temperature, but use ground-state exchange-correlation (XC) functionals. This works well in recent calculations [7, 8], where inclusion of such effects is crucial for accurate prediction. This assumes that finite-temperature effects on exchange-correlation are negligible relative to the KS contributions, which may not always be true.

In the present work we establish the basic rules that will allow the building of finite-temperature exchange-correlation functionals beyond these standard approximations[11].

Central to the thermodynamic description of many-electron systems is the grand-canonical potential, defined as the statistical average of the grand-canonical operator

$$\hat{\Omega} = \hat{H} - \tau \hat{S} - \mu \hat{N}, \quad (1)$$

where \hat{H} , \hat{S} , \hat{N} , τ and μ are the Hamiltonian, entropy, and particle-number operators, temperature and chemical potential, respectively. In detail, $\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}$, where \hat{T} and \hat{V}_{ee} are the kinetic energy and the Coulomb electron-electron interaction operators, and \hat{V} represents an external scalar potential $v(\mathbf{r})$. The entropy operator is given by $\hat{S} = -k \ln \hat{\Gamma}$, where k is the Boltzmann constant and $\hat{\Gamma} = \sum_{N,i} w_{N,i} |\Psi_{N,i}\rangle \langle \Psi_{N,i}|$ is a statistical operator, with $|\Psi_{N,i}\rangle$ and $w_{N,i}$ being orthonormal N -particle states and statistical weights,

respectively, with the latter satisfying the (normalization) condition $\sum_{N,i} w_{N,i} = 1$. The statistical average of an operator \hat{A} is obtained as

$$A[\hat{\Gamma}] = \text{Tr} \{ \hat{\Gamma} \hat{A} \} = \sum_N \sum_i w_{N,i} \langle \Psi_{N,i} | \hat{A} | \Psi_{N,i} \rangle. \quad (2)$$

To create a DFT at finite temperature, Mermin [10] rewrites this as (in modern parlance)

$$\Omega_{v-\mu}^\tau = \min_n \left\{ F^\tau[n] + \int d^3r n(\mathbf{r}) (v(\mathbf{r}) - \mu) \right\} \quad (3)$$

where the minimizing $n(\mathbf{r})$ is the equilibrium density $n^0(\mathbf{r})$, and

$$F^\tau[n] := \min_{\hat{\Gamma} \rightarrow n} F^\tau[\hat{\Gamma}] = \min_{\hat{\Gamma} \rightarrow n} \left\{ T[\hat{\Gamma}] + V_{\text{ee}}[\hat{\Gamma}] - \tau S[\hat{\Gamma}] \right\}, \quad (4)$$

is the finite-temperature analog of the universal Hohenberg-Kohn functional, defined through a constrained search [15]. This depends only on τ and not on μ . We denote $\hat{\Gamma}^\tau[n]$ as the minimizing statistical operator in Eq. (4), and define the density functionals:

$$\begin{aligned} T^\tau[n] &:= T[\hat{\Gamma}^\tau[n]], & V_{\text{ee}}^\tau[n] &:= V_{\text{ee}}[\hat{\Gamma}^\tau[n]], \\ S^\tau[n] &:= S[\hat{\Gamma}^\tau[n]], & K^\tau[n] &:= T[\hat{\Gamma}^\tau[n]] - \tau S[\hat{\Gamma}^\tau[n]]. \end{aligned}$$

i.e., each density functional is the trace of its operator over the minimizing $\hat{\Gamma}$ for the given τ and density. Because it arises so often in this work, we have defined the "kentropy" $K^\tau[n]$.

Next consider a system of non-interacting electrons at the same temperature τ , and denote its one-body potential as $v_s(\mathbf{r})$. All the previous considerations apply, and we choose $v_s(\mathbf{r})$ to make its density match that of the interacting problem. This defines the KS system at finite temperature. The corresponding functionals will be labeled with the subscript s .

We have found that the exchange (x) and correlation (c) parts of the grand-canonical potential, as well as the kentropy and the potential energy (U) are bound to fulfil the exact inequalities[11]:

$$\Omega_x^\tau[n] \leq 0, \quad \Omega_c^\tau[n] \leq 0, \quad U_c^\tau[n] \leq 0, \quad K_c^\tau[n] \geq 0, \quad (5)$$

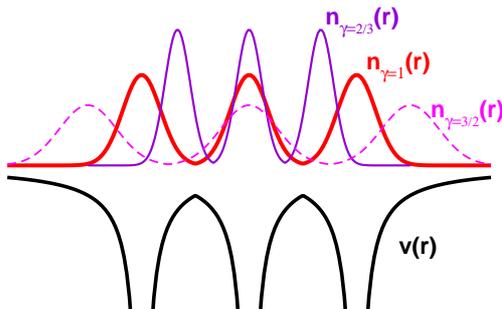
and no approximation should violate these basic rules.

Some of the most important results in ground-state DFT come from uniform scaling of the coordinates[17]. In the following considerations, when we refer explicitly to wavefunctions, we shall restrict to wavefunctions having finite norm on their entire domain of definition.

Under norm-preserving homogeneous scaling of the coordinate $\mathbf{r} \rightarrow \gamma\mathbf{r}$, with $\gamma > 0$, to the scaled wave function [17]

$$\Psi^\gamma(\mathbf{r}_1, \dots, \mathbf{r}_N) := \gamma^{\frac{3}{2}N} \Psi(\gamma\mathbf{r}_1, \dots, \gamma\mathbf{r}_N), \quad (6)$$

corresponds the scaled density $n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r})$. A simple 1D sketch of the scaling procedure is given in this figure:



Writing $\Psi^\gamma(\mathbf{r}_1, \dots, \mathbf{r}_N) = \langle \mathbf{r}_1, \dots, \mathbf{r}_N | \Psi^\gamma \rangle$ in terms of the (representation-free) element $|\Psi^\gamma\rangle$ of Hilbert space, the scaled statistical operator is defined as[11]

$$\hat{\Gamma}_\gamma := \sum_N \sum_i w_{N,i} |\Psi_{N,i}^\gamma\rangle \langle \Psi_{N,i}^\gamma|, \quad (7)$$

where the statistical weights are hold fixed, i.e., the scaling only acts on the states.

With the above definition, the statistical average of an operator whose pure-state expectation value scales homogeneously [17], scales homogeneously as well. In particular, we have: $T[\hat{\Gamma}_\gamma] = \gamma^2 T[\hat{\Gamma}]$, $V_{\text{ee}}[\hat{\Gamma}_\gamma] = \gamma V_{\text{ee}}[\hat{\Gamma}]$, $N[\hat{\Gamma}_\gamma] = N[\hat{\Gamma}]$, and $S[\hat{\Gamma}_\gamma] = S[\hat{\Gamma}]$. The scaling behavior of the *density* functionals is, however, more subtle. First consider the non-interacting functionals in some detail. We observe that

$$\hat{\Gamma}_s^\tau[n_\gamma] = \hat{\Gamma}_{s,\gamma}^{\tau/\gamma^2}[n], \quad (8)$$

which implies that

$$F_s^\tau[n_\gamma] = \gamma^2 F_s^{\tau/\gamma^2}[n] \quad , \quad S_s^\tau[n_\gamma] = S_s^{\tau/\gamma^2}[n]. \quad (9)$$

For non-interacting electrons, the statistical operator at a given temperature that is the minimizer for a given *scaled* density is simply the scaled statistical operator, but at a quadratically *scaled* temperature, an effect that is obviously absent in the ground-state theory.

Next, we consider the interacting case. The analysis of the scaling relations allows to derive a set of inequalities that provide tight constraints on the functionals, and are used in non-empirical functional construction in the ground state. We obtain the following:

$$\Omega_{\text{x}}^{\tau}[n_{\gamma}] = \gamma \Omega_{\text{x}}^{\tau/\gamma^2}[n]. \quad (10)$$

$$K_{\text{c}}^{\tau}[n_{\gamma}] \leq \gamma^2 K_{\text{c}}^{\tau/\gamma^2}[n], \quad U_{\text{c}}^{\tau}[n_{\gamma}] \geq \gamma U_{\text{c}}^{\tau/\gamma^2}[n]. \quad (11)$$

$$\Omega_{\text{c}}^{\tau}[n_{\gamma}] \geq \gamma \Omega_{\text{c}}^{\tau/\gamma^2}[n], \quad \gamma \geq 1, \quad (12)$$

which are reversed if $\gamma < 1$.

Lastly, we consider the adiabatic coupling constant for finite temperature, its relationship to scaling, and derive the adiabatic connection formula. Define

$$F^{\tau,\lambda}[n] := \min_{\hat{\Gamma} \rightarrow n} \left\{ T[\hat{\Gamma}] + \lambda V_{\text{ee}}[\hat{\Gamma}] - \tau S[\hat{\Gamma}] \right\}, \quad (13)$$

with $\hat{\Gamma}^{\tau,\lambda}[n]$ being the corresponding minimizing $\hat{\Gamma}$.

Of course, non-interacting functionals are not affected by a coupling constant modification. Eq. (10) implies that the exchange and Hartree density functionals have a linear dependence on λ . Employing the minimization property of Eq. (13) and the Hellmann-Feynman theorem, we find[11]

$$\Omega_{\text{xc}}^{\tau}[n] = \int_0^1 d\lambda U_{\text{xc}}^{\tau}[n](\lambda), \quad (14)$$

where

$$U_{\text{xc}}^{\tau}[n](\lambda) = V_{\text{ee}}[\hat{\Gamma}^{\tau,\lambda}[n]] - U^{\tau}[n]. \quad (15)$$

Eq. (14) is the finite-temperature adiabatic connection formula, whose zero-temperature limit played a central role in ground-state DFT. $U_{\text{xc}}^{\tau}[n](0) = \Omega_{\text{x}}^{\tau}[n] < 0$ (Eq. 5), and the scaling inequalities can be combined, analogously to Ref. [17], to show that $U_{\text{xc}}^{\tau}[n](\lambda)$ is monotonically decreasing in λ , as shown in the schematic drawing below.

So far, all results presented have been exact. To see them in practice, consider the finite-temperature local density approximation (LDA) to $\Omega_{\text{xc}}^{\tau}[n]$

$$\Omega_{\text{xc}}^{\text{LDA}\tau}[n] = \int d^3r \omega_{\text{xc}}^{\text{unif}\tau}(n(\mathbf{r})), \quad (16)$$

where $\omega_{\text{xc}}^{\text{unif}\tau}(n)$ is the XC grand canonical potential density of a uniform electron gas of density n . Because a *uniform* electron gas is a quantum mechanical system, its energies satisfy

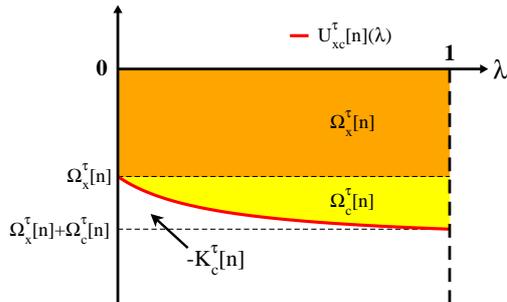


FIG. 1: Geometrical interpretation of the adiabatic connection formula. The shaded area between the curve and the λ axis represents $\Omega_{XC}^\tau[n]$. All magnitudes are negative, in agreement with the inequalities in Eq.(5).

all our conditions, guaranteeing by construction that LDA satisfies all the exact conditions listed here. In the Jacob's ladder of functional construction [13], more sophisticated approximations should also satisfy these conditions. To give one simple example of the usefulness of our results, Eq. (10) implies

$$\omega_x^{\text{unif}\tau}(n(\mathbf{r})) = e_x^{\text{unif}}(n(\mathbf{r})) F_x(\tilde{\tau}(\mathbf{r})), \quad (17)$$

where $e_x^{\text{unif}}(n(\mathbf{r})) = -A_x n^{4/3}(\mathbf{r})$, $A_x = (3/4\pi)(3\pi^2)^{1/3}$, and $\tilde{\tau}(\mathbf{r}) = \tau/n^{2/3}(\mathbf{r})$ is a dimensionless measure of the local temperature. Thus the largest fractional deviations from ground-state results should occur (in LDA) in regions of lowest density, but these contribute less in absolute terms.

In summary, there is a present lack of approximate density functionals for finite temperature. We have derived many basic relations needed to construct such approximations, and expect future approximations to either build these in, or be tested against them. In principle, such approximations should already be implemented in high-temperature DFT calculations, at least at the LDA level, as a check that XC corrections due to finite temperature do not alter calculated results. If they do, then more accurate approximations than LDA will be needed to account for them.

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