Exact Conditions in Finite-Temperature Density-Functional Theory

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Exact conditions in finite temperature density functional theory

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Density functional theory (DFT) for electrons at finite temperature is increasingly important in condensed matter and chemistry. Exact conditions that have proven crucial in constraining and constructing accurate approximations for ground-state DFT are generalized to finite temperature, including the adiabatic connection formula. We discuss consequences for functional construction.

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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, 5] and superconducting phase transitions [6, 7], shock waves [8, 9], warm dense matter [10], and hot plasmas [11–13].

Within density functional theory, the natural framework for treating such effects was created by Mermin [14, 15]. 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 [8, 10], 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.

The uniform electron gas at finite temperature (also called the one-component plasma) has been well-studied, and has in the past provided the natural starting point for DFT studies of such finite-temperature XC effects, as input into the local density approximation (LDA) at finite T [16]. However, the LDA is too inaccurate for most modern applications of DFT, and almost all recent calculations use a generalized gradient approximation or hybrid with exchange [17]. The errors of LDA would typically be enormous relative to the temperature corrections we seek, especially for correlation, and so could lead to quite misleading results. Accurate calculation of finite temperature contributions requires accurate approximate functionals. Magnetic phase transitions bear an additional difficulty: The low-lying excitations are collective, i.e., magnons whose description requires non-collinear version of spin-DFT. Hence, a finite-temperature version of spin-DFT involving only spin-up and spin-down densities and thus only spin-flip excitations, is bound to fail in predicting, e.g., the critical temperature [4].

The most fundamental steps toward both understanding a functional and creating accurate approximations are deriving its inequalities from the variational definition of the functional. These yield both the signs of energy contributions and, via uniform scaling of the spatial coordinates, basic equalities and inequalities that non-empirical functionals should satisfy by construction. The adiabatic connection formula [18] is intimately related. Here, we (i) establish components of the fundamental functional needed for treating finite temperature, (ii) prove the most basic properties (signs of the energy contributions), (iii) show that the temperature must be scaled simultaneously with the spatial coordinate, (iv) derive the inequalities under such scaling, and (v) give the adiabatic connection formula for finite temperature. These results establish the basic rules for all finite-temperature KS treatments.

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

$$\hat{\Omega} = \hat{H} - \tau\hat{S} - \mu\hat{N}, \tag{1}$$

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, $\hat{H} = \hat{T} + \hat{V}_{\text{ee}} + \hat{V}$, where $\hat{T}$ and $\hat{V}_{\text{ee}}$ 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

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

The thermodynamical equilibrium properties of many-electron systems are obtained from the knowledge of the grand-canonical statistical operator $\hat{\Gamma}^0 = \sum_{N,i} w^0_{N,i} |\Psi^0_{N,i}\rangle\langle\Psi^0_{N,i}|$, where $|\Psi^0_{N,i}\rangle$ are the N-particle eigenstates of $\hat{H}$ with energies $E^0_{N,i}$, and the equilibrium statistical weights are given by $w^0_{N,i} = \frac{\exp[-\beta(E^0_{N,i}-\mu N)]}{\sum_{N,i}\exp[-\beta(E^0_{N,i}-\mu N)]}$, where $\beta = \frac{1}{k\tau}$ [19]. The Gibbs principle ensures that $\hat{\Gamma}^0$ minimizes the statistical average of the grand-potential operator. We emphasize that $\hat{\Gamma}^0$ is unique [14] and that in the limit of zero temperature, for systems with degenerate ground states, it leads to ensembles with equal statistical weights.

To create a DFT at finite temperature, Mermin [14] rewrites this as (in modern parlance)

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

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

$$F^\tau[n] := \min_{\hat{\Gamma}\to n} F^\tau[\hat{\Gamma}] = \min_{\hat{\Gamma}\to n} \left\{ T[\hat{\Gamma}] + V_{\rm ee}[\hat{\Gamma}] - \tau S[\hat{\Gamma}] \right\}, \tag{4}$$

is the finite-temperature analog of the universal Hohenberg-Kohn functional, defined through a constrained search [19, 20]. 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:

$$\begin{aligned} T^\tau[n] &:= T[\hat{\Gamma}^\tau[n]], \quad V^\tau_{\rm ee}[n] := V_{\rm ee}[\hat{\Gamma}^\tau[n]], \\ S^\tau[n] &:= S[\hat{\Gamma}^\tau[n]], \end{aligned} \tag{5}$$

i.e., each density functional is the trace of its operator over the minimizing $\hat{\Gamma}$ for the given τ and density.

Next consider a system of non-interacting electrons at the same temperature τ, and denote its one-body potential as $v_{\rm S}(\mathbf{r})$. All the previous arguments apply, and we choose $v_{\rm S}(\mathbf{r})$ to make its density match that of the interacting problem. This defines the KS system at finite temperature. Because it arises so often in this work, we define the kentropy as

$$K^\tau[\hat{\Gamma}] := T[\hat{\Gamma}] - \tau\, S[\hat{\Gamma}], \tag{6}$$

and we show it plays an analogous role to the kinetic energy in ground-state DFT, to which it reduces as $\tau \to 0$. The non-interacting functional is just

$$F^\tau_{\rm S}[n] := \min_{\hat{\Gamma}\to n} K^\tau[\hat{\Gamma}] = K^\tau[\hat{\Gamma}^\tau_{\rm S}[n]] \tag{7}$$

from Eq. (4) applied without $V_{\rm ee}$, and we define:

$$T^\tau_{\rm S}[n] := T[\hat{\Gamma}^\tau_{\rm S}[n]], \quad S^\tau_{\rm S}[n] := S[\hat{\Gamma}^\tau_{\rm S}[n]]. \tag{8}$$

Next we define the difference functionals that are crucial to the KS method. Write

$$V^\tau_{\rm ee,s}[n] := V_{\rm ee}[\hat{\Gamma}^\tau_{\rm S}[n]] = U^\tau[n] + \Omega^\tau_{\rm X}[n], \tag{9}$$

where $U^\tau[n]$ in terms of the density has the form of the usual Hartree energy, and expressing $\Omega^\tau_{\rm X}[n]$ in terms of the module square of the one-body density matrix stemming from $\hat{\Gamma}^\tau_{\rm S}[n]$ [21] we observe that $\Omega^\tau_{\rm X}[n] \le 0$.

The kinetic correlation is

$$T^\tau_{\rm C}[n] := T[\hat{\Gamma}^\tau[n]] - T[\hat{\Gamma}^\tau_{\rm S}[n]], \tag{10}$$

and similarly define $S^\tau_{\rm C}[n]$ and $K^\tau_{\rm C}[n]$, while the potential contribution is

$$U^\tau_{\rm C}[n] := V_{\rm ee}[\hat{\Gamma}^\tau[n]] - V_{\rm ee}[\hat{\Gamma}^\tau_{\rm S}[n]]. \tag{11}$$

The sum of the energy components is, as in ground-state DFT, the correlation energy, $E^\tau_{\rm C}[n] := T^\tau_{\rm C}[n] + U^\tau_{\rm C}[n]$, while the grand-canonical correlation potential is

$$\Omega^\tau_{\rm C}[n] := K^\tau_{\rm C}[n] + U^\tau_{\rm C}[n] = E^\tau_{\rm C}[n] - \tau S^\tau_{\rm C}[n], \tag{12}$$

and $\Omega^\tau_{\rm XC}[n] := \Omega^\tau_{\rm X}[n] + \Omega^\tau_{\rm C}[n]$.

We now prove the most basic theorems about the signs of our quantities. To show that the correlation-kentropy (or kentropic correlation) is always positive, begin by noting $K^\tau[\hat{\Gamma}^\tau_{\rm S}[n]] \le K^\tau[\hat{\Gamma}^\tau[n]]$, because $\hat{\Gamma}^\tau_{\rm S}[n]$ minimizes $K^\tau[\hat{\Gamma}]$. By inserting the definition, Eq. (6), we find $K^\tau_{\rm C}[n] \ge 0$, with equality only when the interaction is zero. It is the kentropic correlation that is guaranteed to be positive, not the kinetic correlation alone, contrary to the pure ground-state case[22]. Similarly, since $F^\tau[\hat{\Gamma}^\tau[n]] \le F^\tau[\hat{\Gamma}^\tau_{\rm S}[n]]$, we find $\Omega^\tau_{\rm C}[n] \le 0$. Combining these results with Eq. (12) implies $U^\tau_{\rm C}[n] \le 0$. Thus

$$\Omega^\tau_{\rm X}[n] \le 0,\ \Omega^\tau_{\rm C}[n] \le 0,\ U^\tau_{\rm C}[n] \le 0,\ K^\tau_{\rm C}[n] \ge 0, \tag{13}$$

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[22, 23]. 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 $\mathbf{r} \to \gamma\mathbf{r}$, with $\gamma > 0$, to the scaled wave function [22]

$$\Psi^\gamma(\mathbf{r}_1, ..., \mathbf{r}_N) := \gamma^{\frac{3}{2}N}\Psi(\gamma\mathbf{r}_1, ..., \gamma\mathbf{r}_N), \tag{14}$$

corresponds the scaled density $n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r})$. Writing $\Psi^\gamma(\mathbf{r}_1, ..., \mathbf{r}_N) = \langle \mathbf{r}_1, ..., \mathbf{r}_N|\Psi^\gamma\rangle$ in terms of the (representation-free) element $|\Psi^\gamma\rangle$ of Hilbert space, the scaled statistical operator is defined as

$$\hat{\Gamma}_\gamma := \sum_N \sum_i w_{N,i} |\Psi^\gamma_{N,i}\rangle\langle\Psi^\gamma_{N,i}|, \tag{15}$$

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 [22], scales homogeneously as well. In particular, we have: $T[\hat{\Gamma}_\gamma] = \gamma^2 T[\hat{\Gamma}]$, $V_{\rm ee}[\hat{\Gamma}_\gamma] = \gamma V_{\rm ee}[\hat{\Gamma}]$,

$N[\hat\Gamma_\gamma] = N[\hat\Gamma]$, 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. Because $\hat\Gamma^\tau_{\rm S}[n]$ minimizes K^τ, Eq. (7), and

$$K^\tau[\hat\Gamma_\gamma] = \gamma^2 \left(T[\hat\Gamma] - \frac{\tau}{\gamma^2}\, S[\hat\Gamma] \right) = \gamma^2 K^{\tau/\gamma^2}[\hat\Gamma]\ , \tag{16}$$

then

$$\hat\Gamma^\tau_{\rm S}[n_\gamma] = \hat\Gamma^{\tau/\gamma^2}_{{\rm S},\gamma}[n]\ , \qquad F^\tau_{\rm S}[n_\gamma] = \gamma^2\, F^{\tau/\gamma^2}_{\rm S}[n]\ . \tag{17}$$

In particular we notice that

$$S^\tau_s[n_\gamma] = S^{\tau/\gamma^2}_s[n]\ . \tag{18}$$

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 *scaled* temperature, an effect that is obviously absent in the ground-state theory.

There are further simple implications. First, if we invert the sense of Eq. (17), we can write:

$$F^{\tau'}_{\rm S}[n] = \frac{\tau'}{\tau}\, F^\tau_{\rm S}[n_{\sqrt{\tau/\tau'}}], \tag{19}$$

i.e., knowledge of $F^\tau_{\rm S}[n]$ at any one finite τ generates *its entire temperature dependence*, via scaling. Furthermore, it must always collapse to the ground-state KS kinetic energy under scaling to the high-density limit:

$$T_{\rm S}[n] = \lim_{\gamma\to\infty} F^\tau_{\rm S}[n_\gamma]/\gamma^2. \tag{20}$$

Similarly, in the low-density limit

$$S^\infty_{\rm S}[n] = -\lim_{\gamma\to 0} F^\tau_{\rm S}[n_\gamma]/\tau, \tag{21}$$

where $S^\infty_{\rm S}[n]$ is the non-interacting KS entropy in the high-temperature limit.

Next, we consider the interacting case. The exchange contribution is much simpler than correlation, because it is extracted from the one-particle density matrix. Because $V_{\rm ee}[\hat\Gamma]$ and $U[\hat\Gamma]$ scale linearly with γ, and using the simple scaling relation for $\hat\Gamma_{\rm S}$, Eq. (17),

$$\Omega^\tau_{\rm X}[n_\gamma] = \gamma\, \Omega^{\tau/\gamma^2}_{\rm X}[n]\ . \tag{22}$$

This scaling result is important in ground-state DFT, where it restricts the dependence of the exchange-enhancement factor to depending on just the reduced density gradient [23]. But the more interesting case is correlation. From the definition, Eq. (4),

$$F^\tau[n_\gamma] \le F^\tau[\hat\Gamma^{\tau'}_\gamma[n]]\ , \tag{23}$$

since $\hat\Gamma^{\tau'}_\gamma[n]$ has density n_γ, and τ' is *any* temperature. Using the scaling properties and choosing $\tau' = \tau/\gamma^2$, then the fundamental inequality of scaling is

$$K^\tau[n_\gamma] + V^\tau_{\rm ee}[n_\gamma] \le \gamma^2\, K^{\tau/\gamma^2}[n] + \gamma\, V^{\tau/\gamma^2}_{\rm ee}[n]. \tag{24}$$

To find a condition on the kentropy alone, define $n'(\mathbf{r}) = n_\gamma(\mathbf{r})$, $\gamma' = 1/\gamma$, and $\tau' = \tau/\gamma^2$ in Eq. (24). Multiply the result by γ', and combine with Eq. (24), to find

$$K^\tau[n_\gamma] \le \gamma^2\, K^{\tau/\gamma^2}[n], \qquad \gamma \ge 1\ . \tag{25}$$

This is the finite temperature analog of the subquadratic scaling of the kinetic energy in the real system [22]. Another combination isolates the repulsive contributions:

$$V^\tau_{\rm ee}[n_\gamma] \ge \gamma\, V^{\tau/\gamma^2}_{\rm ee}[n], \qquad \gamma \ge 1\ . \tag{26}$$

These inequalities loosely constrain the behavior of these large energies. Much more important is to subtract out KS quantities that scale simply, to find for $\gamma \ge 1$:

$$K^\tau_{\rm C}[n_\gamma] \le \gamma^2\, K^{\tau/\gamma^2}_{\rm C}[n], \qquad U^\tau_{\rm C}[n_\gamma] \ge \gamma\, U^{\tau/\gamma^2}_{\rm C}[n]. \tag{27}$$

One more application of Eq. (24) yields

$$\Omega^\tau_{\rm C}[n_\gamma] \ge \gamma\, \Omega^{\tau/\gamma^2}_{\rm C}[n], \qquad \gamma \ge 1, \tag{28}$$

the fundamental scaling inequality for the correlation contribution to the grand canonical potential. The inequalities, Eqs. (25-28), which are reversed if $\gamma < 1$, provide tight constraints on these functionals and are routinely used in non-empirical functional construction in the ground state[23]. For example, combining Eq. (22) with Eq. (28) in the high-density limit, yields:

$$\Omega^\tau_{\rm X}[n] = \lim_{\gamma\to\infty} \Omega^{\gamma^2\tau}_{\rm XC}[n_\gamma]/\gamma. \tag{29}$$

This scaling procedure can usually be applied easily to any approximate $\Omega^\tau_{\rm XC}[n]$ to extract its separate exchange and correlation contributions.

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

$$F^{\tau,\lambda}[n] = \min_{\hat\Gamma\to n} \left\{ T[\hat\Gamma] + \lambda\, V_{\rm ee}[\hat\Gamma] - \tau S[\hat\Gamma] \right\}\ , \tag{30}$$

with $\hat\Gamma^{\tau,\lambda}[n]$ being the corresponding minimizing $\hat\Gamma$. By scaling, it is straightforward to show:

$$\hat\Gamma^{\tau,\lambda}[n] = \hat\Gamma^{\tau/\lambda^2}_\lambda[n_{1/\lambda}]\ , \qquad F^{\tau,\lambda}[n] = \lambda^2\, F^{\tau/\lambda^2}[n_{1/\lambda}]\ . \tag{31}$$

where quantities with one superscript are evaluated at $\lambda = 1$. Eq. (31) is the interacting generalization of Eq. (17) and shows that, even in the presence of interactions, simple equalities are possible, but at the price of altering the coupling constant. In particular we notice that

$$S^{\tau,\lambda}[n] = S^{\tau/\lambda^2}[n_{1/\lambda}]\ . \tag{32}$$

Of course, non-interacting functionals are not affected by a coupling constant modification. Eq. (22) implies that the exchange and Hartree density functionals have a linear dependence on λ. Employing the minimization property of Eq. (30) and the Hellmann-Feynman theorem, we find

$$\Omega^{\tau}_{\rm XC}[n] = \int_0^1 d\lambda\, U^{\tau}_{\rm XC}[n](\lambda) \;, \tag{33}$$

where

$$U^{\tau}_{\rm XC}[n](\lambda) = V_{\rm ee}[\hat{\Gamma}^{\tau,\lambda}[n]] - U^{\tau}[n] \;. \tag{34}$$

Eq. (33) is the finite-temperature adiabatic connection formula, whose zero-temperature limit played a central role in ground-state DFT. $U^{\tau}_{\rm XC}[n](0) = \Omega^{\tau}_{\rm X}[n] < 0$ (Eq.(13)), and the scaling inequalities can be combined, analogously to Ref. [22], to show that $U^{\tau}_{\rm XC}[n](\lambda)$ is monotonically decreasing in λ.

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

$$\Omega^{\rm LDA\tau}_{\rm XC}[n] = \int d^3r\, \omega^{\rm unif\tau}_{\rm XC}(n(\mathbf{r})) \;, \tag{35}$$

where $\omega^{\rm unif\tau}_{\rm XC}(n)$ 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 all our conditions, guaranteeing by construction that LDA satisfies all the exact conditions listed here. In the Jacob's ladder of functional construction [17], more sophisticated approximations should also satisfy these conditions. To give one simple example, Eq. (22) implies

$$\omega^{\rm unif\tau}_{\rm X}(n(\mathbf{r})) = e^{\rm unif}_{\rm X}(n(\mathbf{r}))\, F_{\rm X}(\tilde{\tau}(\mathbf{r})) \;, \tag{36}$$

where $e^{\rm unif}_{\rm X}(n(\mathbf{r})) = -A_{\rm X}\; n^{4/3}(\mathbf{r})$, $A_{\rm X} = (3/4\pi)(3\pi^2)^{1/3}$, 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. For a generalized gradient approximation (GGA), Eq. (22) implies

$$\omega^{\rm GGA\tau}_{\rm X}(n(\mathbf{r}), |\nabla n|(\mathbf{r})) = e^{\rm unif}_{\rm X}(n(\mathbf{r}))\, F_{\rm X}(s(\mathbf{r}), \tilde{\tau}(\mathbf{r})), \tag{37}$$

where the dimensionless gradient s is $|\nabla n|/(2k_F n)$ and $k_F = (3\pi^2 n)^{1/3}$, i.e., the exchange enhancement factor $F_{\rm X}(s, \tilde{\tau})$ depends on the temperature only via $\tilde{\tau}$.

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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