



Scaling, bounds, and inequalities for the noninteracting density functionals at finite temperature

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Finite-temperature density functional theory requires representations for the internal energy, entropy, and free energy as functionals of the local density field. A central formal difficulty for an orbital-free representation is the construction of the corresponding functionals for noninteracting particles in an arbitrary external potential. That problem is posed here in the context of the equilibrium statistical mechanics of an inhomogeneous system. The density functionals are defined and shown to be equal to the extremal state for a functional of the reduced one-particle statistical operators. Convexity of the latter functionals implies a class of general inequalities. First, it is shown that the familiar von Weizsäcker lower bound for zero temperature functionals applies at finite temperature as well. An upper bound is obtained in terms of a single-particle statistical operator corresponding to the Thomas-Fermi approximation. Next, the behavior of the density functionals under coordinate scaling is obtained. The inequalities are exploited to obtain a class of upper and lower bounds at constant temperature, and a complementary class at constant density. The utility of such constraints and their relationship to corresponding results at zero temperature are discussed.

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I. INTRODUCTION

Density functional theory (DFT) is an important structure for posing problems of equilibrium many-body physics in a nonperturbative context. Most applications, with many significant successes, have been in the extremes of zero-temperature ground-state systems¹⁻⁷ or high-temperature classical systems⁸⁻¹⁰. Shortly after the ground-state Hohenberg-Kohn-Sham formulation, a finite-temperature generalization was given¹¹, but it has attracted far less development than the ground-state version¹². Recently, attention has been directed toward systems in a difficult intermediate domain known as “warm dense matter.” Extensions of existing density functional approaches (including procedures to develop approximate functionals nonempirically) to this domain have met with challenges. One is the temperature dependence itself of the functionals. Another is technical, associated with solving a self-consistent single-particle eigenvalue problem (the Kohn-Sham equation) for which a growing number of eigenvalues and eigenfunctions (orbitals) is required as the temperature is increased at solid densities. For many applications, such as determining forces for Born-Oppenheimer molecular dynamics of ions in warm dense matter, this growth produces a computational bottleneck. The Kohn-Sham procedure is not intrinsic to DFT, so an alternative approach is to return to the expression of the entire free energy as a functional of the density. Once known, the extremum condition of DFT becomes a single nonlinear, nonlocal equation for the density whose solution replaces that constructed from the Kohn-Sham orbitals and eigenfunctions. Solving that Euler equation is facilitated by introducing the Kohn-Sham separation into a noninteracting functional, which is presumably dominant, and the remainder, but without introducing orbital-dependent expressions. This approach is known as orbital free DFT (OFDFT). An example is given

by the Thomas-Fermi-Dirac model, which is a local density approximation.

A critical component for OFDFT is the free energy density functional for an inhomogeneous but noninteracting system. The objective here is to define the free energy, energy, and entropy density functionals for a noninteracting system at finite temperature in forms suitable for constructing approximations. (Note the correspondence with the ground-state theory, namely, the definition of the Kohn-Sham kinetic energy and exact exchange energy.) To aid in that construction important exact constraints are obtained here as well. These include scaling laws, upper and lower bounds, and inequalities. Development and use of such constraints is promising in light of the history of analogous developments in zero-temperature DFT.

The approach here is to exploit the relationship of DFT to the equilibrium statistical mechanics of nonuniform systems. (The relationship of DFT to thermodynamics and Legendre transforms is discussed in Refs. 13–19.) The variational context of DFT is simply related to the extremal properties of the ensembles representing equilibrium systems. In the next section, thermodynamics is described in the grand ensemble, for which the thermodynamic variables are the temperature T and chemical potential μ . The presence of an external single-particle potential $v(\mathbf{r})$ transforms the chemical potential to a local function $\tilde{\mu}(\mathbf{r}) = \mu - v(\mathbf{r})$. A change of thermodynamic variables $T, \tilde{\mu}(\mathbf{r})$ to temperature and density $T, n(\mathbf{r})$ is effected by an appropriate Legendre transformation. The resulting thermodynamic functionals of $T, n(\mathbf{r})$ are the desired density functionals for DFT. The extremum condition of DFT is simply the thermodynamic identity relating the functional derivative of the free energy to the chemical potential.

This context for DFT is described briefly in the next section and then specialized to the noninteracting system in Sec. III. The equation for the density provides the definition of the

local chemical potential as a functional of the density. The free energy, energy, and entropy are represented in terms of the equilibrium single-particle reduced density matrix, or Fermi operator. The latter depends on the chemical potential, so that in this way these properties are identified as functionals of the density through the chemical potential. Next, corresponding functionals of an arbitrary single-particle statistical operator are defined. Using convexity of the free energy functional of statistical operators, it is shown that the minimum occurs for the Fermi operator, resulting in the free energy density functional being a minimum for the free energy statistical operator functionals. This is the source for the inequalities described subsequently.

In Sec. IV, the transformation of the density functionals under coordinate scaling is obtained from dimensional analysis. An alternative constructive derivation which connects explicitly with ground-state uniform scaling^{20–22} is given in Appendix B. Next, the familiar von Weizsäcker lower bound on the kinetic energy for zero-temperature DFT^{23–25} is shown to hold for finite temperature as well. (Observe that both Ayers²⁶ and Sagvolden and Perdew²⁷ had proved the von Weizsäcker lower bound for general ensembles, hence implicitly for finite temperature.) A statistical operator underlying the Thomas-Fermi approximation for the density is defined via an appropriate Wigner function representation and used to obtain an upper bound for the free energy. Finally, two classes of inequalities are established for all density functionals using the scaling laws. One is for fixed temperature at different densities, while the other is for fixed density and different temperatures. For the case of differential scaling, the results reduce to differentials of equilibrium thermodynamics.

In the last section these results are discussed and their utility for constraint-based approximations described.

II. EQUILIBRIUM STATISTICAL MECHANICS FOR A NONUNIFORM SYSTEM

While treatment of a homogeneous noninteracting Fermion system is a textbook staple, the statistical mechanics of inhomogeneous noninteracting systems is less well documented. The formal structure of ensemble DFT has been discussed in diverse forms^{14,19,28–33} since Ref. 11. Some of those formulations resemble the ground-state theory more than others. Homogeneous scaling at finite temperature has been treated recently in a manner closely related to ground-state scaling³⁴. The present approach is complementary to those, in the sense of providing a close, systematic connection with statistical mechanical methods widely used in the treatment of electronically hot systems, (e.g., plasmas). To set notation and make the context explicit, we begin with a brief summary of the relevant statistical mechanics.

The system of interest is comprised of N electrons in a uniform, rigid, neutralizing background (“one component plasma,” “jellium,” “electron gas”)³⁵, and in an external potential v . The Hamiltonian is

$$\hat{H} = \hat{H}_e + \sum_{\alpha=1}^N v(\hat{\mathbf{q}}_{\alpha}). \quad (1)$$

A caret over a symbol indicates that it is an operator. Here

$$\begin{aligned} \hat{H}_e = & \sum_{\alpha=1}^N \frac{\hat{p}_{\alpha}^2}{2m_{\alpha}} + \frac{1}{2} \sum_{\alpha \neq \gamma=1}^N \frac{e^2}{|\hat{\mathbf{q}}_{\alpha} - \hat{\mathbf{q}}_{\gamma}|} - \sum_{\alpha=1}^N \int d\mathbf{r} \frac{n_b e^2}{|\hat{\mathbf{q}}_{\alpha} - \mathbf{r}|} \\ & + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n_b^2 e^2}{|\mathbf{r} - \mathbf{r}'|}. \end{aligned} \quad (2)$$

The integrations extend over the volume V and n_b is the average number density of the background chosen for overall charge neutrality (see discussion below). The first two terms are the kinetic energy and electron-electron Coulomb interaction energies. The third term is the interaction energy of the electrons with the average neutralizing background (charge density $n_b e$), while the last term is the interaction energy among elements of that uniform background. The origin and necessity for this neutralizing background arises from the long-range nature of the Coulomb potential—a macroscopic equilibrium state for the electrons alone does not exist³⁶. Charge neutrality is a necessity for thermodynamic stability (e.g., systems of both electrons and positive ions). The system considered here is a model for electrons in such two-component systems, where the uniform, rigid, neutralizing background assures that thermodynamics exists^{37,38}. The use of the average neutralizing background anticipates the use of the grand canonical ensemble. The electron density operator is defined as

$$\hat{n}(\mathbf{r}) = \sum_{\alpha=1}^N \delta(\mathbf{r} - \hat{\mathbf{q}}_{\alpha}). \quad (3)$$

Note that

$$\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}') = \sum_{\alpha \neq \gamma=1}^N \delta(\mathbf{r} - \hat{\mathbf{q}}_{\alpha})(\mathbf{r}' - \hat{\mathbf{q}}_{\gamma}) + \delta(\mathbf{r} - \mathbf{r}')\hat{n}(\mathbf{r}). \quad (4)$$

Then Eq. (1) becomes

$$\begin{aligned} \hat{H} = & \sum_{\alpha=1}^N \frac{\hat{p}_{\alpha}^2}{2m_{\alpha}} + \int d\mathbf{r} v(\mathbf{r})\hat{n}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \\ & \times [(\hat{n}(\mathbf{r}) - n_b)(\hat{n}(\mathbf{r}') - n_b) - \delta(\mathbf{r} - \mathbf{r}')n_b]. \end{aligned} \quad (5)$$

The problem of interest is to determine the equilibrium electron density $n(\mathbf{r})$ and the thermodynamics for this inhomogeneous electron gas.

The thermodynamic properties for this class of inhomogeneous systems are determined in the grand canonical ensemble as functions of the inverse temperature $\beta = 1/k_B T$ and functionals of the local chemical potential

$$\tilde{\mu}(\mathbf{r}) = \mu - v(\mathbf{r}), \quad (6)$$

which combines the external potential $v(\mathbf{r})$ with the constraint on average total particle number, the constant chemical potential μ . The fundamental thermodynamic potential for this ensemble, $\Omega(\beta | \tilde{\mu})$, is related simply to the pressure

$$\begin{aligned} \Omega(\beta | \tilde{\mu}) = & -p(\beta | \tilde{\mu})V \\ = & -\beta^{-1} \ln \sum_{N=0}^{\infty} \text{Tr}^{(N)} e^{-\beta[\hat{H}_e - \int d\mathbf{r} \tilde{\mu}(\mathbf{r})\hat{n}(\mathbf{r})]}. \end{aligned} \quad (7)$$

The trace extends over the Hilbert space for N electrons. The notation $(\beta | \tilde{\mu})$ indicates variable dependence and functional dependence, respectively. The thermodynamical average electron density as a function of β and functional of $\tilde{\mu}(r)$ follows directly as

$$n(\mathbf{r}, \beta | \tilde{\mu}) = - \frac{\delta \Omega(\beta | \tilde{\mu})}{\delta \tilde{\mu}(\mathbf{r})} \Big|_{\beta}. \quad (8)$$

Similarly, the internal energy is determined from the derivative with respect to β

$$U(\beta | \tilde{\mu}) = \frac{\partial \beta \Omega(\beta | \beta^{-1} \tilde{\mu}')}{\partial \beta} \Big|_{\tilde{\mu}'}, \quad \tilde{\mu}' = \beta \tilde{\mu}. \quad (9)$$

Now consider a change of variables from $\beta, \tilde{\mu}(\mathbf{r})$ to $\beta, n(\mathbf{r})$ by a Legendre transformation to the free energy

$$F(\beta | n) = \Omega(\beta | \tilde{\mu}) + \int d\mathbf{r} \tilde{\mu}(\mathbf{r}) n(\mathbf{r}). \quad (10)$$

By construction $F(\beta | n)$ is independent of $\tilde{\mu}(r)$ [i.e., $\delta F(\beta | n) / \delta \tilde{\mu}(r) = 0$]. Therefore it is “universal” in the sense that the functional $F(\beta | \cdot)$ is the same for all external potentials, with its argument evaluated at the corresponding different density fields. In all of the following, only density fields $n(\mathbf{r}, \beta | \tilde{\mu})$ that can be represented by a chemical potential $\tilde{\mu}(\mathbf{r})$ as in Eqs. (7) and (8) are considered. These are the $\tilde{\mu}$ -representable physical densities of thermodynamics. The corresponding ground-state theory requirement on the density is v representability. With this restriction on the class of densities, Eqs. (7) and (8) provide the constructive definition for the free energy functional: Calculate $\Omega(\beta | \tilde{\mu})$ as a functional of $\tilde{\mu}$ from its explicit definition; invert Eq. (8) for the chemical potential as a functional of the density $\tilde{\mu}(r, \beta | n)$; substitute $\tilde{\mu}(r, \beta | n)$ into the right side of Eq. (10).

The functional derivative of $F(\beta | n)$ gives the inverse of Eq. (8)

$$\tilde{\mu}(\mathbf{r}, \beta | n) = \frac{\delta F(\beta | n)}{\delta n(\mathbf{r})} \Big|_{\beta}. \quad (11)$$

This is an identity which expresses the one-one relationship of a $\tilde{\mu}(\mathbf{r})$ with a specific density $n(\mathbf{r})$. However, it also can be viewed as an equation to find the density associated with a given $\tilde{\mu}(\mathbf{r})$. For example, consider the case where $\tilde{\mu}_0(\mathbf{r})$ is given, and the objective is to find the corresponding $n_0(\mathbf{r})$. This can be accomplished by solving the equation

$$\tilde{\mu}_0(\mathbf{r}) = \frac{\delta F(\beta | n)}{\delta n(\mathbf{r})} \Big|_{\beta}. \quad (12)$$

The unique solution is $n(\mathbf{r}) = n_0(\mathbf{r})$. This is no longer an identity, but an equation to be solved: Equality holds *only* for the particular density $n_0(\mathbf{r})$.

Up to here the development is simply equilibrium quantum statistical mechanics. But the same result follows from DFT in an equivalent way. In terms of the stipulated local chemical potential $\tilde{\mu}_0(\mathbf{r})$, ensemble constrained search³⁹ enables us to define the functional

$$\Omega_{\tilde{\mu}_0}(\beta | n) \equiv F(\beta | n) - \int d\mathbf{r} \tilde{\mu}_0(\mathbf{r}) n(\mathbf{r}). \quad (13)$$

The condition for an extremum of $\Omega_{\tilde{\mu}_0}(\beta | n)$ gives Eq. (12) as its Euler equation

$$\frac{\delta \Omega_{\tilde{\mu}_0}(\beta | n)}{\delta n(\mathbf{r})} \Big|_{\beta} = 0 \Rightarrow \tilde{\mu}_0(\mathbf{r}) = \frac{\delta F(\beta | n)}{\delta n(\mathbf{r})} \Big|_{\beta}. \quad (14)$$

From Eqs. (10) and (12) note that

$$\Omega_{\tilde{\mu}_0}(\beta | n) = \Omega(\beta | \tilde{\mu}) - \int d\mathbf{r} [\tilde{\mu}_0(\mathbf{r}) - \tilde{\mu}(\mathbf{r}, \beta | n)] n(\mathbf{r}), \quad (15)$$

and so

$$\Omega_{\tilde{\mu}_0}(\beta | n_0) = \Omega(\beta | \tilde{\mu}_0). \quad (16)$$

The case of primary interest is an external potential due to a given configuration of ions

$$v_0(\mathbf{r}) = \mu - \mu_0(\mathbf{r}) = -Ze^2 \int d\mathbf{r}' \frac{[\hat{n}(\mathbf{r}) - n_e] \hat{n}_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (17)$$

$$\hat{n}_i(\mathbf{r}) = \sum_{\alpha=1}^{N_i} \delta(\mathbf{r} - \hat{\mathbf{R}}_{i\alpha}),$$

where Z is the ion charge number, and $ZN_i = N$. For simplicity, we discuss only a single ionic species; generalization is obvious.

Determination of the electron density field for given ion configurations [hence, given $\tilde{\mu}_0(\mathbf{r})$] involves constructing $F(\beta | n)$ and solving Eq. (14) for $n_0(\mathbf{r})$. The thermodynamic properties then are determined from $F(\beta | n_0)$. The problem of constructing $F(\beta | n)$ is separated into two parts: finding the corresponding functional for noninteracting electrons (but in the external fields of the ions), $F^{(0)}(\beta | n)$, and finding the functional associated with the contribution from Coulomb interactions, $\Delta F(\beta | n)$. This is a logical separation, since $F^{(0)}(\beta | n)$ is itself a universal functional, with properties similar to $F(\beta | n)$. For example, there is a unique functional $\tilde{\mu}^{(0)}(\mathbf{r}, \beta | n)$ associated with $F^{(0)}(\beta | n)$ for each n given by

$$\tilde{\mu}^{(0)}(\mathbf{r}, \beta | n) = \frac{\delta F^{(0)}(\beta | n)}{\delta n(\mathbf{r})} \Big|_{\beta}. \quad (18)$$

The notation $\tilde{\mu}^{(0)}$ specifies that the functional is that for the noninteracting relationship, with the same chemical potential and external potential

$$\tilde{\mu}^{(0)}(\mathbf{r}, \beta | n) = \mu - v(\mathbf{r}). \quad (19)$$

The Coulomb contributions $\Delta F(\beta | n)$ (“excess free energy” in statistical mechanical usage) conventionally are divided into a mean-field (Hartree) contribution plus a remainder, the exchange-correlation contribution

$$\Delta F(\beta | n) = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' n(\mathbf{r}) \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}') + F_{xc}(\beta | n), \quad (20)$$

so that the total free energy is composed as

$$F(\beta | n) = F^{(0)}(\beta | n) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' n(\mathbf{r}) \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}') + F_{xc}(\beta | n). \quad (21)$$

With these definitions Eq. (14) becomes (with an overall factor of β included to make the equations dimensionless)

$$\beta\tilde{\mu}^{(0)}(\mathbf{r}, \beta | n) = \beta\tilde{\mu}_0(\mathbf{r}) - \beta e^2 \int d\mathbf{r}' n(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} - \beta \left. \frac{\delta F_{xc}(\beta | n)}{\delta n(\mathbf{r})} \right|_{\beta}. \quad (22)$$

Again, this relationship does not hold for all n . Rather, it is an equation to be solved for $n = n_0$. Its solution can be addressed in two ways. The Kohn-Sham approach is suggested by combining Eqs. (14), (18), and (21) in a form equivalent to Eq. (22)

$$\left. \frac{\delta F^{(0)}(\beta | n)}{\delta n(\mathbf{r})} \right|_{\beta} = \mu - v_{KS}(\mathbf{r}, \beta | n), \quad (23)$$

where the Kohn-Sham (KS) potential v_{KS} is identified as

$$v_{KS}(\mathbf{r}, \beta | n) = v_0(\mathbf{r}) + e^2 \int d\mathbf{r}' n(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \left. \frac{\delta F_{xc}(\beta | n)}{\delta n(\mathbf{r})} \right|_{\beta}. \quad (24)$$

Equation (23) has the form of a noninteracting Fermi system in the external potential v_{KS} . The density and all other thermodynamic properties then are determined from the self-consistent single-particle Hamiltonian eigenvalue problem

$$\left(\frac{\hat{p}^2}{2m} + v_{KS}(\mathbf{r}, \beta | n) \right) \phi_{\alpha} = \epsilon_{\alpha} \phi_{\alpha}, \quad (25)$$

$$n = \sum_{\alpha} (e^{\beta(\epsilon_{\alpha} - \mu)} + 1)^{-1} |\phi_{\alpha}(\mathbf{r})|^2.$$

Note that, in this approach, explicit construction of the functionals $F^{(0)}(\beta | n)$ and $\tilde{\mu}^{(0)}(\mathbf{r}, \beta | n)$ is avoided, at the cost of introducing the KS orbital manifold, an issue already mentioned. The alternative is to construct these functionals, then to solve Eq. (22) directly as an equation for n , and use its solution in Eq. (21) to determine the free energy. This second method is OFDFT; it avoids construction of the Kohn-Sham eigenfunctions and eigenvalues. Of course, when properly implemented the two approaches are equivalent.

In the context of OFDFT, the remainder of this discussion is restricted to the determination of $F^{(0)}(\beta | n)$ and $\beta\tilde{\mu}^{(0)}(\mathbf{r}, \beta | n)$. A suitable determination of the corresponding exchange-correlation functionals is a separate problem not considered here.

III. FUNCTIONALS FOR THE NONINTERACTING SYSTEM

A. Functionals of the density

Without Coulomb interactions, the Hamiltonian of Eq. (4) is a sum of single-particle Hamiltonians. Consequently, the evaluation of the grand potential (7) can be reduced to a single-particle problem. For completeness, the analysis is sketched in Appendix A, with the result

$$\Omega^{(0)}(\beta | \tilde{\mu}) = -\beta^{-1} \text{Tr} \ln (1 + e^{-\beta [\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{q}})]}), \quad (26)$$

$$\tilde{\mu}(\hat{\mathbf{q}}) = \mu - v(\hat{\mathbf{q}}).$$

The trace is now taken over the single-particle Hilbert space (spin is not considered here for simplicity). The density is obtained by Eq. (8) (see also Appendix A)

$$n(\mathbf{r}, \beta | \tilde{\mu}) = - \left. \frac{\delta \Omega^{(0)}(\beta | \tilde{\mu})}{\delta \tilde{\mu}(\mathbf{r})} \right|_{\beta} = \text{Tr} \delta(\mathbf{r} - \hat{\mathbf{q}}) \hat{\rho}_e, \quad (27)$$

where the one-body reduced equilibrium statistical operator (hereafter referred to as the ‘‘Fermi operator’’) is

$$\hat{\rho}_e = (e^{\beta [\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{q}})]} + 1)^{-1}. \quad (28)$$

The central observation at this point is that Eq. (27) defines the one-to-one relationship of $\tilde{\mu}(\mathbf{q})$ to an associated density

$$\tilde{\mu}(\mathbf{q}) = \tilde{\mu}^{(0)}(\mathbf{q}, \beta | n). \quad (29)$$

A special case is the relationship for a uniform external potential for which $\tilde{\mu}^{(0)}(\mathbf{q}, \beta | n) \rightarrow \mu_e^{(0)}(\beta, n)$, which is the familiar relationship of the chemical potential to density for the ideal Fermi gas. The functional $\tilde{\mu}^{(0)}(\mathbf{q}, \beta | \cdot)$ is universal (i.e., it is the same for all external potentials). The use of Eq. (29) in Eq. (28) expresses the Fermi operator as a universal (operator-valued) functional of the density as well

$$\hat{\rho}_e = \hat{\rho}_e(\beta | n) = (e^{\beta [\frac{\hat{p}^2}{2m} - \tilde{\mu}^{(0)}(\hat{\mathbf{q}}, \beta | n)]} + 1)^{-1}. \quad (30)$$

The free energy for the noninteracting system is obtained from $\Omega^{(0)}(\beta | \tilde{\mu})$ by the Legendre transformation, Eq. (10), as

$$\beta F^{(0)}(\beta | n) = -\text{Tr} [\ln (1 + e^{-\beta [\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{q}})]}) - \beta \tilde{\mu}(\hat{\mathbf{q}}) \hat{\rho}_e], \quad (31)$$

where use has been made of Eq. (27) for the density. This result can be expressed in terms of the Fermi operator by eliminating $\tilde{\mu}(\hat{\mathbf{q}})$ using Eq. (28) to get

$$\beta F^{(0)}(\beta | n) = \text{Tr} \left[(1 - \hat{\rho}_e) \ln(1 - \hat{\rho}_e) + \hat{\rho}_e \ln \hat{\rho}_e + \beta \frac{\hat{p}^2}{2m} \hat{\rho}_e \right]. \quad (32)$$

Finally, entropy and internal energy functionals can be identified from the definition

$$F^{(0)} = U^{(0)} - T S^{(0)}, \quad (33)$$

to get

$$U^{(0)}(\beta | n) = \text{Tr} \frac{\hat{p}^2}{2m} \hat{\rho}_e, \quad (34)$$

$$S^{(0)}(\beta | n) = -k_B \text{Tr} [(1 - \hat{\rho}_e) \ln(1 - \hat{\rho}_e) + \hat{\rho}_e \ln \hat{\rho}_e]. \quad (35)$$

Since the spectrum of $\hat{\rho}_e$ is real and in the interval (0, 1), the energy and entropy are positive. Observe that all functional dependence upon the density occurs through the Fermi operator in the form of Eq. (30).

This development delineates the essential task, which is to expose these definitions as explicit functionals of the density. Consider, for example, the determination of $\tilde{\mu}^{(0)}(\mathbf{q}, \beta | n)$ from inversion of the density equation (27). Evaluating the trace in coordinate representation gives

$$n(\mathbf{r}) = \langle \mathbf{r} | (e^{\beta [\frac{\hat{p}^2}{2m} - \tilde{\mu}^{(0)}(\hat{\mathbf{q}}, \beta | n)]} + 1)^{-1} | \mathbf{r} \rangle. \quad (36)$$

This expression is deceptively simple since the extraction of $\tilde{\mu}^{(0)}$ is complicated by the noncommutation of $\tilde{\mu}^{(0)}(\hat{\mathbf{q}}, \beta | n)$ with the kinetic energy. A common *approximation* is the Thomas-Fermi form, which is obtained by replacing the operator $\tilde{\mu}^{(0)}(\hat{\mathbf{q}}, \beta | n)$ by the c-number $\tilde{\mu}^{(0)}(\mathbf{r}, \beta | n)$, so that the Fermi operator becomes diagonal in momentum representation

$$n(\mathbf{r}) \rightarrow h^{-3} \int d\mathbf{p} (e^{\beta[\frac{p^2}{2m} - \tilde{\mu}^{(0)}(\mathbf{r}, \beta | n)]} + 1)^{-1}. \quad (37)$$

In this case, the inversion is the same as that for the uniform ideal Fermi gas noted above $\tilde{\mu}^{(0)}(\mathbf{r}, \beta | n) \rightarrow \mu_e^{(0)}[\beta, n(\mathbf{r})]$. This inversion is exact in the uniform limit, but conditions for its validity otherwise are not known. In the following discussion, several exact properties of the density functionals are exposed to provide guidance and constraints on approximations for their explicit forms.

B. Functionals of the statistical operator

To put the equilibrium functionals of the last section in context, it is useful to define related functionals of trace class operators $\hat{\rho}$ which are Hermitian, positive, and have spectrum on $(0, 1)$ but otherwise are arbitrary. For them, define

$$\beta \mathcal{F}^{(0)}(\beta | \hat{\rho}) \equiv \text{Tr} \left[(1 - \hat{\rho}) \ln(1 - \hat{\rho}) + \hat{\rho} \ln \hat{\rho} + \beta \frac{\hat{p}^2}{2m} \hat{\rho} \right], \quad (38)$$

$$\mathcal{U}^{(0)}[\hat{\rho}] = \text{Tr} \frac{\hat{p}^2}{2m} \hat{\rho}, \quad (39)$$

$$\mathcal{S}^{(0)}[\hat{\rho}] = -k_B \text{Tr} [(1 - \hat{\rho}) \ln(1 - \hat{\rho}) + \hat{\rho} \ln \hat{\rho}]. \quad (40)$$

Clearly these functionals become the density functionals of the preceding section when evaluated at the Fermi operator, $\hat{\rho} = \hat{\rho}_e$. More generally, $\mathcal{F}^{(0)}(\beta | \hat{\rho})$ is a convex functional of $\hat{\rho}$ while $\mathcal{S}^{(0)}[\hat{\rho}]$ is positive and concave. Furthermore, the minimum of $\mathcal{F}^{(0)}(\beta | \hat{\rho})$ occurs for $\hat{\rho} = \hat{\rho}_e$, among all $\hat{\rho}$ with the same density

$$n(\mathbf{r}) = \text{Tr} \delta(\hat{\mathbf{q}} - \mathbf{r}) \hat{\rho}. \quad (41)$$

To see this evaluate

$$\delta \left(\mathcal{F}^{(0)}(\beta | \hat{\rho}) + \int d\mathbf{r} \lambda(\mathbf{r}) [n(\mathbf{r}) - \text{Tr} \delta(\hat{\mathbf{q}} - \mathbf{r}) \hat{\rho}] \right) = 0, \quad (42)$$

where $\lambda(\mathbf{r})$ is a Lagrange multiplier function. The solution is

$$\hat{\rho}_m = (e^{\beta[\frac{p^2}{2m} + \lambda(\hat{\mathbf{q}})]} + 1)^{-1} = \hat{\rho}_e. \quad (43)$$

The last equality follows since $\lambda(\hat{\mathbf{q}})$ must be determined from Eq. (41), which is the same as Eq. (27). In summary,

$$F^{(0)}(\beta | n) = \mathcal{F}^{(0)}(\beta | \hat{\rho}_e) \leq \mathcal{F}^{(0)}(\beta | \hat{\rho}). \quad (44)$$

This result will be used below to establish upper bounds on the free energy density functional.

IV. SCALING RELATIONS, BOUNDS, AND INEQUALITIES

A. Scaling from dimensional analysis

In this section scaling properties of the functionals are obtained from dimensional analysis. An alternative constructive

derivation of scaling properties is given in Appendix B. It is closer in formulation to the uniform scaling widely used in ground-state DFT²⁰, but does not expose the simplicity and profound connection with thermodynamics that comes from the dimensional approach.

All the density dependence of the density functionals occurs through the dependence of the Fermi operator on $\tilde{\mu}^{(0)}(\mathbf{r}, \beta | n)$ or, equivalently, the dimensionless local ‘‘activity’’

$$v^{(0)}(\mathbf{r}, \beta | n) \equiv \beta \tilde{\mu}^{(0)}(\mathbf{r}, \beta | n). \quad (45)$$

Define the dimensionless momentum and position operators

$$\hat{y} \equiv \sqrt{\frac{\beta}{2m}} \hat{p}, \quad \mathbf{r}^* = \frac{\mathbf{r}}{\lambda}, \quad (46)$$

where λ is the thermal de Broglie wavelength,

$$\lambda = \left(\frac{2\pi\beta\hbar^2}{m} \right)^{1/2}. \quad (47)$$

Then Eq. (36) becomes

$$n^*(\mathbf{r}^*) \equiv \lambda^3 n(\mathbf{r}) = \langle \mathbf{r}^* | (e^{\hat{y}^2 - v(\hat{\mathbf{r}})} + 1)^{-1} | \mathbf{r}^* \rangle. \quad (48)$$

This shows that $v(\hat{\mathbf{r}})$ is a functional of the dimensionless density $n^*(\mathbf{r}^*)$ alone

$$v(\mathbf{r}) = v^{(0)}(\mathbf{r}, \beta | n) = v^{(0)}(\mathbf{r}^* | n^*). \quad (49)$$

The immediate consequence of Eq. (49) is that the Fermi operator and all functionals in dimensionless form are also functionals of n^* only, namely,

$$\beta F^{(0)}(\beta | n) = F^*[n^*], \quad \beta U^{(0)}(\beta | n) = U^*[n^*], \quad (50)$$

$$\frac{1}{k_B} \mathcal{S}^{(0)}(\beta | n) = S^*[n^*].$$

Consider now the scaling transformation

$$\mathbf{r} \rightarrow \gamma \mathbf{r}, \quad n(\mathbf{r}) d\mathbf{r} \rightarrow \gamma^3 n(\gamma \mathbf{r}) d\mathbf{r}, \quad V \rightarrow \gamma^{-3} V, \quad (51)$$

where V is the volume. This transformation preserves the total number of particles

$$\int_V n(\mathbf{r}) d\mathbf{r} = N = \int_{\gamma^{-3}V} \gamma^3 n(\gamma \mathbf{r}) d\mathbf{r}. \quad (52)$$

The dimensionless density then transforms according to

$$n^*(\mathbf{r}^*) \equiv \lambda^3 n(\mathbf{r}) \rightarrow \gamma^3 \lambda^3 n(\gamma \mathbf{r}) = (\gamma \lambda)^3 n(\gamma \lambda \mathbf{r}^*). \quad (53)$$

This is the expected result, namely that the length scale λ used to define the dimensionless density itself has been scaled by γ . However, this scaling can be canceled by a suitable scaling of the temperature in the de Broglie wavelength, namely

$$\gamma \lambda (\gamma^{-2} \beta) = \lambda (\beta). \quad (54)$$

Thus, a combined scaling transformation of lengths *and* of the temperature leaves the dimensionless density invariant, and hence all the functionals of Eq. (50), unchanged. To be explicit, define the transformed density by

$$n_\gamma(\mathbf{r}) \equiv \gamma^3 n(\gamma \mathbf{r}). \quad (55)$$

Then from Eq. (50) and the invariance of n^* , the desired scaling properties follow

$$F^{(0)}(\beta | n) = \gamma^{-2} F^{(0)}(\gamma^{-2} \beta | n_\gamma), \quad (56)$$

$$U^{(0)}(\beta | n) = \gamma^{-2} U^{(0)}(\gamma^{-2} \beta | n_\gamma),$$

$$S^{(0)}(\beta | n) = S^{(0)}(\gamma^{-2} \beta | n_\gamma). \quad (57)$$

B. Bounds and inequalities

In this section specific upper and lower bounds are described. In addition, the scaling laws are used to obtain inequalities for the various functionals for different values of their arguments (temperature and density).

1. Lower bound

It is well known^{23–25} that the noninteracting kinetic energy density functional at zero temperature is bounded from below by the von Weizsäcker functional

$$U_{vW}[n] \equiv \frac{\hbar^2}{8m} \int d\mathbf{r} \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})} = \frac{\hbar^2}{2m} \int d\mathbf{r} |\nabla \varphi(\mathbf{r})|^2. \quad (58)$$

The last equality is obtained by introducing the square root of the density (a positive function)

$$n(\mathbf{r}) = \varphi(\mathbf{r})^2. \quad (59)$$

We now show explicitly that the von Weizsäcker functional is a lower bound for the kinetic energy density functional at finite temperature as well. This result may be anticipated as a consequence of the proofs^{26,27} that the bound holds in ensemble DFT.

Since $\hat{\rho}_e$ is a Hermitian, positive operator it has a square root

$$\hat{\rho}_e = (\hat{\psi})^2. \quad (60)$$

Then $U^{(0)}(\beta | n)$ from Eq. (34) can be written

$$U^{(0)}(\beta | n) = \frac{1}{2m} \text{Tr} |\hat{\rho} \hat{\psi}|^2 = \frac{\hbar^2}{2m} \int d\mathbf{r} d\mathbf{r}' |\nabla \langle \mathbf{r} | \hat{\psi} | \mathbf{r}' \rangle|^2. \quad (61)$$

Note the similarity of this exact result to the approximate von Weizsäcker result (58) (the relationship of $\hat{\psi}$ to the square root of the density is $\varphi(\mathbf{r}) = \sqrt{\langle \mathbf{r} | \hat{\psi}^2 | \mathbf{r} \rangle}$). To extract the von Weizsäcker contribution, define

$$X(\mathbf{r}, \mathbf{r}') \equiv \varphi^{-1}(\mathbf{r}) \langle \mathbf{r} | \hat{\psi} | \mathbf{r}' \rangle. \quad (62)$$

Then

$$\begin{aligned} U^{(0)}(\beta | n) &= \frac{\hbar^2}{2m} \int d\mathbf{r} |\nabla \varphi(\mathbf{r})|^2 \int d\mathbf{r}'' |X(\mathbf{r}, \mathbf{r}'')|^2 \\ &+ \frac{\hbar^2}{2m} \int d\mathbf{r} |\varphi(\mathbf{r})|^2 \int d\mathbf{r}'' |\nabla X(\mathbf{r}, \mathbf{r}'')|^2 \\ &+ \frac{\hbar^2}{2m} \int d\mathbf{r} \varphi(\mathbf{r}) \nabla \varphi(\mathbf{r}) \nabla \int d\mathbf{r}'' |X(\mathbf{r}, \mathbf{r}'')|^2. \end{aligned} \quad (63)$$

But

$$\int d\mathbf{r}'' |X(\mathbf{r}, \mathbf{r}'')|^2 = \frac{1}{n(\mathbf{r})} \int d\mathbf{r}'' \langle \mathbf{r} | \hat{\psi} | \mathbf{r}'' \rangle \langle \mathbf{r}'' | \hat{\psi} | \mathbf{r} \rangle = 1, \quad (64)$$

so

$$\begin{aligned} U^{(0)}(\beta | n) &= \frac{\hbar^2}{2m} \int d\mathbf{r} |\nabla \varphi(\mathbf{r})|^2 + \frac{\hbar^2}{2m} \int d\mathbf{r} |\varphi(\mathbf{r})|^2 \\ &\times \int d\mathbf{r}'' |\nabla X(\mathbf{r}, \mathbf{r}'')|^2 \\ &\geq U_{vW}[n]. \end{aligned} \quad (65)$$

This is the desired result, showing that U_{vW} is a lower bound for $U^{(0)}$. The analog in ground-state DFT is the so-called Pauli-term decomposition^{40–43} of the KS kinetic energy

$$\mathcal{T}_s = \mathcal{T}_{vW} + \mathcal{T}_\theta, \quad \mathcal{T}_\theta \geq 0. \quad (66)$$

Equation (65) also provides a bound for the free energy functional, namely

$$F(\beta | n) \geq U_{vW}[n] - TS(\beta | n). \quad (67)$$

In obtaining Eq. (65), no use has been made of the integral over \mathbf{r} , so provided that no traceless forms are added to the energy densities, the bound holds for them too

$$F(\beta | n) \equiv \int d\mathbf{r} f(\mathbf{r}, \beta | n), \quad U(\beta | n) \equiv \int d\mathbf{r} u(\mathbf{r}, \beta | n), \quad (68)$$

$$S(\beta | n) \equiv \int d\mathbf{r} s(\mathbf{r}, \beta | n),$$

$$\begin{aligned} u(\mathbf{r}, \beta | n) &= u_{vW}(\mathbf{r} | n) + \frac{\hbar^2}{2m} n(\mathbf{r}) \int d\mathbf{r}'' |\nabla X(\mathbf{r}, \mathbf{r}'')|^2 \\ &\geq u_{vW}(\mathbf{r} | n), \end{aligned} \quad (69)$$

$$f(\mathbf{r}, \beta | n) \geq u_{vW}(\mathbf{r} | n) - Ts(\mathbf{r}, \beta | n). \quad (70)$$

2. Upper bound

Upper bounds are provided by Eq. (44) if a suitable choice for $\hat{\rho}$ can be found. In practice, it is common to use the local density approximation, which in this context leads to the Thomas-Fermi form for the density. The question arises as to what statistical operator corresponds to the Thomas-Fermi approximation. More specifically, what $\hat{\rho}$ has the Thomas-Fermi form for the density? The necessary condition is

$$\langle \mathbf{r} | \hat{\rho}_{TF} | \mathbf{r} \rangle = h^{-3} \int d\mathbf{p} (e^{\beta \{ \frac{p^2}{2m} - \mu_e[\beta, n(\mathbf{r})] \}} + 1)^{-1}. \quad (71)$$

However, this condition determines only the diagonal matrix elements of $\hat{\rho}_{TF}$. To fix the statistical operator definitively, consider its associated Wigner distribution $n_{TF}(p, \mathbf{R})$, defined by

$$\langle \mathbf{r} | \hat{\rho}_{TF} | \mathbf{r}' \rangle = \frac{1}{h^3} \int d\mathbf{p} e^{i\mathbf{p} \cdot \mathbf{q}} n_{TF}(p, \mathbf{R}), \quad (72)$$

$$\mathbf{R} = \frac{\mathbf{r} + \mathbf{r}'}{2}, \quad \mathbf{q} = \mathbf{r} - \mathbf{r}'.$$

Specialization to $\mathbf{q} = \mathbf{0}$ and comparison with Eq. (71) determines $n_{TF}(p, \mathbf{R})$ as

$$n_{TF}(p, \mathbf{R}) = (e^{\beta \{ \frac{p^2}{2m} - \mu_e[\beta, n(\mathbf{r})] \}} + 1)^{-1}. \quad (73)$$

With the statistical operator determined, an upper bound is given by Eq. (44) with $\hat{\rho} = \hat{\rho}_{TF}$

$$F^{(0)}(\beta | n) \leq \mathcal{F}^{(0)}(\beta | \hat{\rho}_{TF}) = \mathcal{U}^{(0)}[\hat{\rho}_{TF}] - TS^{(0)}[\hat{\rho}_{TF}]. \quad (74)$$

The calculation of $\mathcal{U}^{(0)}[\hat{\rho}_{TF}]$ is straightforward

$$\begin{aligned} \mathcal{U}^{(0)}[\hat{\rho}_{TF}] &= -\frac{\hbar^2}{2m} \int d\mathbf{r} [\nabla^2 \langle \mathbf{r} | \hat{\rho}_{TF} | \mathbf{r} \rangle]_{\mathbf{r}=\mathbf{r}} \\ &= \int d\mathbf{r} \frac{1}{h^3} \int d\mathbf{p} \frac{\mathbf{p}^2}{2m} n_{TF}(p, \mathbf{r}) \\ &= \int d\mathbf{r} u_{TF}[\beta, n(\mathbf{r})], \end{aligned} \quad (75)$$

where $u_{TF}[\beta, n(\mathbf{r})]$ is the finite-temperature Thomas-Fermi energy density

$$u_{TF}[\beta, n(\mathbf{r})] = \frac{1}{h^3} \int d\mathbf{p} \frac{\mathbf{p}^2}{2m} (e^{\beta \{ \frac{p^2}{2m} - \mu_e[\beta, n(\mathbf{r})] \}} + 1)^{-1}. \quad (76)$$

To complete the calculation of the upper bound it is necessary to evaluate

$$\begin{aligned} S^{(0)}[\hat{\rho}_{TF}] &= -k_B \int d\mathbf{r} \langle \mathbf{r} | [(1 - \hat{\rho}_{TF}) \ln(1 - \hat{\rho}_{TF}) \\ &\quad + \hat{\rho}_{TF} \ln \hat{\rho}_{TF}] | \mathbf{r} \rangle. \end{aligned} \quad (77)$$

Although the density dependence of all matrix elements of $\hat{\rho}_{TF}$ is explicit, the evaluation of nonlinear functions of this operator is still a difficult problem and the explicit form for Eq. (77) has not yet been determined.

In any event, the upper bound for the free energy density functional is

$$\begin{aligned} F^{(0)}(\beta | n) &\leq \int d\mathbf{r} u_{TF}[\beta, n(\mathbf{r})] + \beta^{-1} \int d\mathbf{r} \langle \mathbf{r} | [(1 - \hat{\rho}_{TF}) \\ &\quad \times \ln(1 - \hat{\rho}_{TF}) + \hat{\rho}_{TF} \ln \hat{\rho}_{TF}] | \mathbf{r} \rangle. \end{aligned} \quad (78)$$

We remark that a naive attempt to get a zero-temperature upper bound by dropping the entropy term in Eq. (74) fails because the resulting expression no longer is convex.

3. Inequalities

A class of inequalities can be obtained from Eq. (44) and the scaling laws. Recall the definition of n_γ in Eq. (55), and choose $\hat{\rho} = \hat{\rho}_e(\gamma^{-2}\beta | n_\gamma)$ in Eq. (44),

$$\begin{aligned} F^{(0)}(\beta | n_\gamma) &= \mathcal{F}^{(0)}[\beta | \hat{\rho}_e(\beta | n_\gamma)] \\ &\leq \mathcal{F}^{(0)}[\beta | \hat{\rho}_e(\gamma^{-2}\beta | n_\gamma)], \end{aligned} \quad (79)$$

and then use the definition of $\mathcal{F}^{(0)}(\beta | \rho)$ to get

$$F^{(0)}(\beta | n_\gamma) - F^{(0)}(\gamma^{-2}\beta | n_\gamma) \leq (\gamma^2 - 1)TS^{(0)}(\gamma^{-2}\beta | n_\gamma). \quad (80)$$

Use of the scaling laws (56) and (57) to convert functions of $\gamma^{-2}\beta$ to corresponding functions of β leads to

$$F^{(0)}(\beta | n_\gamma) - \gamma^2 F^{(0)}(\beta | n) \leq (\gamma^2 - 1)TS^{(0)}(\beta | n). \quad (81)$$

Since the entropy is nonnegative, an inequality for constant temperature and different densities is

$$F^{(0)}(\beta | n_\gamma) \leq \gamma^2 F^{(0)}(\beta | n), \quad \gamma \leq 1. \quad (82)$$

Use of the scaling laws once more to convert $F^{(0)}(\beta | n_\gamma)$ to $\gamma^2 F^{(0)}(\gamma^2\beta | n)$ gives the inequality for constant density

$$F^{(0)}(\gamma^2\beta | n) \leq F^{(0)}(\beta | n), \quad \gamma \leq 1. \quad (83)$$

Repetition of this analysis for the choice

$$\begin{aligned} F^{(0)}(\gamma^{-2}\beta | n_\gamma) &= \mathcal{F}^{(0)}[\gamma^{-2}\beta | \hat{\rho}_e(\gamma^{-2}\beta | n_\gamma)] \\ &\leq \mathcal{F}^{(0)}[\gamma^{-2}\beta | \hat{\rho}_e(\beta | n_\gamma)], \end{aligned} \quad (84)$$

leads to

$$F^{(0)}(\gamma^{-2}\beta | n_\gamma) - F^{(0)}(\beta | n_\gamma) \leq (1 - \gamma^2)TS^{(0)}(\beta | n_\gamma), \quad (85)$$

and scaling gives the reverse inequalities for $\gamma \geq 1$

$$\gamma^2 F^{(0)}(\beta | n) \leq F^{(0)}(\beta | n_\gamma), \quad \gamma \geq 1. \quad (86)$$

In consequence, it also is true that

$$F^{(0)}(\beta | n) \leq F^{(0)}(\gamma^2\beta | n), \quad \gamma \geq 1. \quad (87)$$

Appendix C has a further consideration of Eqs. (80) and (85) to reach the corresponding inequalities for the entropy and energy functionals. The results are summarized in Table I. These inequalities imply that the entropy and energy are monotonically increasing with T , while the free energy is monotonically decreasing with T , at constant n .

Return to Eq. (81) and use scaling to write it as

$$F^{(0)}(\gamma^2\beta | n) - F^{(0)}(\beta | n) \leq \frac{(\gamma^2 - 1)}{\gamma^2} TS^{(0)}(\beta | n). \quad (88)$$

Set $\gamma = 1 + \delta$ with $\delta \rightarrow 0$ to get

$$\left. \frac{dF^{(0)}(\beta | n)}{d\beta} \right|_n = TS^{(0)}(\beta | n). \quad (89)$$

This is a thermodynamic identity, which confirms the fact that the functionals considered here are all derived from the grand potential (26) for a nonuniform system at equilibrium.

V. DISCUSSION

The analysis of density functionals relevant to finite temperature DFT has been placed in the context of equilibrium statistical mechanics for a nonuniform system. The free energy

TABLE I. Scaling properties of the noninteracting free energy, internal energy, and entropy

Constant n	Constant β
$F^{(0)}(\beta n) \begin{matrix} \leq \\ \geq \end{matrix} F^{(0)}(\gamma^2\beta n), \quad \gamma \begin{matrix} \geq \\ \leq \end{matrix} 1$	$F^{(0)}(\beta n_\gamma) \begin{matrix} \geq \\ \leq \end{matrix} \gamma^2 F^{(0)}(\beta n), \quad \gamma \begin{matrix} \geq \\ \leq \end{matrix} 1$
$U^{(0)}(\beta n) \begin{matrix} \leq \\ \geq \end{matrix} U^{(0)}(\gamma^2\beta n), \quad \gamma \begin{matrix} \geq \\ \leq \end{matrix} 1$	$U^{(0)}(\beta n_\gamma) \begin{matrix} \geq \\ \leq \end{matrix} \gamma^2 U^{(0)}(\beta n), \quad \gamma \begin{matrix} \geq \\ \leq \end{matrix} 1$
$S^{(0)}(\beta n) \begin{matrix} \geq \\ \leq \end{matrix} S^{(0)}(\gamma^2\beta n), \quad \gamma \begin{matrix} \geq \\ \leq \end{matrix} 1$	$S^{(0)}(\beta n_\gamma) \begin{matrix} \leq \\ \geq \end{matrix} S^{(0)}(\beta n), \quad \gamma \begin{matrix} \geq \\ \leq \end{matrix} 1$

functional of Eq. (10) is precisely the same as that introduced by Mermin, but obtained here as a thermodynamic change of variables via Legendre transformation. This recognition of the thermodynamic context for DFT is expected to play a more important role when the functionals are parameterized by temperature, than for familiar ground-state DFT. The origin of the density dependence through inversion of the relationship of $n(\mathbf{r})$ to $\tilde{\mu}(\mathbf{r})$ allows a formal representation of all functionals for constructive evaluation: The more general constrained search methods are replaced by an explicit, albeit very difficult, many-body evaluation. The analysis here is restricted to the noninteracting functionals for which that many-body problem can be solved. Nevertheless, the necessary inversion to find $\tilde{\mu}(\mathbf{r}) = \tilde{\mu}^{(0)}(\mathbf{r}, \beta | n)$ remains a difficult mathematical task. Hence, the construction of approximate functionals is required in this case as well. The objective here has been to provide both context and constraints for that process.

The noninteracting functionals of Sec. III are deceptively simple and still defy exact evaluation. However, they are in a form convenient for exposing some of their general properties. Linear coordinate scaling is an example. For it, simple dimensional analysis provides the exact results. The results are analogous to those obtained for ground-state DFT, except the temperature is an additional variable that must scale along with the density. This is an example of a general outcome. Many of the finite-temperature results conform to the obvious expectations from the ground-state theory, but some are not predictable by such extrapolation.

The application of these results includes the determination of the volume dependence of the functionals (see, for example, Chihara and Yamagiwa¹⁷). Identification of the von Weizsäcker lower bound for finite temperature is expected, but the proof also provides a representation for the exact positive correction that may be suitable for further analysis. Upper bounds are provided by noting that all functionals depend on the density through the Fermi operator, and that the free energy is the extremum of a convex functional of constrained single-particle reduced statistical operators $\mathcal{F}^{(0)}(\beta | \hat{\rho})$. As an application, the single-particle reduced statistical operator corresponding to the TF approximation was constructed and shown to yield the TF approximation for a class of functionals, but not for the entropy in particular. Thus TF does not result from some approximate single-particle statistical operator. This will be discussed further elsewhere.

The inequalities of the last section are a consequence of the scaling laws and convexity of the $\mathcal{F}^{(0)}(\beta | \hat{\rho})$. Since the scaling transformations involve both temperature and density, two classes of inequalities are described: Those for functionals at different densities but the same constant temperature, and for the temperature dependence of functionals for constant density. Ultimately, it is expected that such inequalities have an instructive thermodynamic interpretation [see, for example, Eq. (89)].

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APPENDIX A: DETERMINATION OF $\Omega^{(0)}(\beta | \tilde{\mu})$

A. Derivation of Eq. (26)

Development of the thermodynamics for an ideal gas occurs in every textbook on equilibrium quantum statistical mechanics. For completeness, the extension to nonuniform systems to derive Eq. (26) is described briefly here. First write Eq. (7) in the form

$$\Omega^{(0)}(\beta | \tilde{\mu}) = -\beta^{-1} \ln \sum_{N=0}^{\infty} \text{Tr}^{(N)} e^{-\beta [\sum_{i=1}^N a(\hat{\mathbf{q}}_i, \hat{\mathbf{p}}_i)]}, \quad (\text{A1})$$

with the single-particle operator $a(\hat{\mathbf{q}}_i, \hat{\mathbf{p}}_i)$ given by

$$a(\hat{\mathbf{q}}_i, \hat{\mathbf{p}}_i) = \frac{\hat{p}_i^2}{2m} - \tilde{\mu}(\hat{\mathbf{q}}_i). \quad (\text{A2})$$

Since $a(\hat{\mathbf{q}}_i, \hat{\mathbf{p}}_i)$ is a Hermitian operator, it has an associated complete basis set for the single-particle Hilbert space

$$a(\hat{\mathbf{q}}_i, \hat{\mathbf{p}}_i) | \alpha_i \rangle = \varepsilon_{\alpha_i} | \alpha_i \rangle. \quad (\text{A3})$$

Observe that the “ α ” are state labels while the “ i ” are particle indices. The N particle Hilbert space then is spanned by the antisymmetrized product basis $\mathcal{S} | \alpha_1, \dots, \alpha_N \rangle$, and

$$\sum_{i=1}^N a(\hat{\mathbf{q}}_i, \hat{\mathbf{p}}_i) \mathcal{S} | \alpha_1, \dots, \alpha_N \rangle = \left(\sum_{i=1}^N \varepsilon_{\alpha_i} \right) \mathcal{S} | \alpha_1, \dots, \alpha_N \rangle. \quad (\text{A4})$$

These total energy eigenvalues can be specified in an equivalent way in terms of the occupation numbers for a given quantum state

$$\sum_{i=1}^N \varepsilon_{\alpha_i} = \sum_{\alpha} \varepsilon_{\alpha} n_{\alpha}. \quad (\text{A5})$$

The sum on the right side is over all single-particle states, and n_{α} is the number of times the quantum number α occurs in the state $| \alpha_1, \dots, \alpha_N \rangle$, restricted by $\sum_{\alpha} n_{\alpha} = N$.

Since the states are antisymmetrized, there is no meaning to assignment of which particles are in the state with quantum number α , only the total number of particles in that state n_{α} . Consequently, the states can be labeled by $\{n_{\alpha}\}$ instead of $\{\alpha_i\}$

$$\mathcal{S} | \alpha_1, \dots, \alpha_N \rangle \longleftrightarrow | \{n_{\alpha}\} \rangle. \quad (\text{A6})$$

In this occupation number representation, the effects of symmetrization are accounted for since one set of $\{n_{\alpha}\}$ represents all the states generated by permutations. The trace for the grand potential can be carried out in this occupation number representation as follows:

$$\begin{aligned} \Omega^{(0)}(\beta | \tilde{\mu}) &= -\beta^{-1} \ln \sum_{N=0}^{\infty} \sum_{\{n_{\alpha}\}} \langle \{n_{\alpha}\} | e^{-\beta [\sum_{i=1}^N a(\hat{\mathbf{q}}_i, \hat{\mathbf{p}}_i)]} | \{n_{\alpha}\} \rangle \\ &= -\beta^{-1} \ln \sum_{N=0}^{\infty} \prod_{\alpha} \sum_{n_{\alpha}} e^{-\beta \varepsilon_{\alpha} n_{\alpha}} \\ &= -\beta^{-1} \ln \sum_{N=0}^{\infty} \prod_{\alpha} \sum_{n_{\alpha}} e^{-\beta \varepsilon_{\alpha} n_{\alpha}} \delta \left(N, \sum_{\alpha} n_{\alpha} \right). \end{aligned} \quad (\text{A7})$$

Primes over summations over n_α indicate the restriction to $\sum_\alpha n_\alpha = N$, a restriction that is removed in the last equality by the explicit Kronecker delta. The summation over N is then performed first, giving

$$\Omega^{(0)}(\beta | \tilde{\mu}) = -\beta^{-1} \sum_\alpha \ln \sum_{n_\alpha} e^{-\beta \varepsilon_\alpha n_\alpha}. \quad (\text{A8})$$

Fermion occupation numbers are all $n_\alpha = 0, 1$ so

$$\begin{aligned} \Omega^{(0)}(\beta | \tilde{\mu}) &= -\beta^{-1} \sum_\alpha \ln(1 + e^{-\beta \varepsilon_\alpha}) \\ &= -\beta^{-1} \sum_\alpha \langle \alpha_1 | \ln(1 + e^{-\beta a(\hat{q}_1 \cdot \hat{p}_1)}) | \alpha_1 \rangle \\ &= -\beta^{-1} \text{Tr} \ln(1 + e^{-\beta a(\hat{q}_1 \cdot \hat{p}_1)}). \end{aligned} \quad (\text{A9})$$

This is the result quoted in Eq. (26).

B. Proof of $n(\mathbf{r}) = -\delta\Omega^{(0)}(\beta | \tilde{\mu})/\delta\tilde{\mu}(\mathbf{r}) |_\beta$

The functional derivatives entail use of some operator algebra. To illustrate this, the derivation of Eq. (27) from Eq. (26) is described. Begin with the functional derivative of Eq. (26),

$$\left. -\frac{\delta\Omega^{(0)}(\beta | \tilde{\mu})}{\delta\tilde{\mu}(\mathbf{r})} \right|_\beta = \beta^{-1} \text{Tr}^{(1)} \frac{\delta}{\delta\tilde{\mu}(\mathbf{r})} \ln(1 + e^{-\beta[\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{q})]}). \quad (\text{A10})$$

To calculate the derivative of the logarithm a useful representation is

$$\ln(1 + \hat{X}) = \int_0^1 d\lambda \partial_\lambda \ln(1 + \lambda \hat{X}) = \int_0^1 d\lambda (1 + \lambda \hat{X})^{-1} \hat{X}, \quad (\text{A11})$$

where

$$\hat{X} = e^{-\beta[\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{r}}, \beta|n)]}. \quad (\text{A12})$$

The functional derivative is then

$$\frac{\delta}{\delta\tilde{\mu}(\mathbf{r})} \ln(1 + \hat{X}) = \int_0^1 d\lambda (1 + \lambda \hat{X})^{-1} \frac{\delta\hat{X}}{\delta\tilde{\mu}(\mathbf{r})} (1 + \lambda \hat{X})^{-1}. \quad (\text{A13})$$

In the present context, this expression occurs under a trace, so use of the cyclic invariance of the trace gives

$$\begin{aligned} \left. -\frac{\delta\Omega^{(0)}(\beta | \tilde{\mu})}{\delta\tilde{\mu}(\mathbf{r})} \right|_\beta &= \beta^{-1} \text{Tr} \int_0^1 d\lambda (1 + \lambda \hat{X})^{-2} \frac{\delta\hat{X}}{\delta\tilde{\mu}(\mathbf{r})} \\ &= \beta^{-1} \text{Tr} (1 + \hat{X})^{-1} \frac{\delta\hat{X}}{\delta\tilde{\mu}(\mathbf{r})}. \end{aligned} \quad (\text{A14})$$

Next, the derivative of the exponential (A12) can be defined as

$$\frac{\delta e^{-\beta(\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{r}})}}{\delta\tilde{\mu}(\mathbf{r})} \equiv \lim_{\beta} \frac{e^{-\beta(\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{r}}) - \delta\tilde{\mu})} - e^{-\beta(\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{r}})}}{\beta\delta\tilde{\mu}(\mathbf{r})}. \quad (\text{A15})$$

Then writing

$$\begin{aligned} e^{-\beta(\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{r}}) - \delta\tilde{\mu}(\hat{\mathbf{r}}))} &\equiv e^{-x(\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{r}}) - \delta\tilde{\mu}(\hat{\mathbf{r}}))} \Big|_{x=\beta}, \\ e^{-x(\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{r}}) - \delta\tilde{\mu}(\hat{\mathbf{r}}))} &= e^{-x(\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{r}}))} U(x, \delta\tilde{\mu}), \end{aligned} \quad (\text{A16})$$

an equation for $U(x, \delta\tilde{\mu})$ is obtained

$$\partial_x U(x, \delta\tilde{\mu}) = e^{x(\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{r}}))} \delta\tilde{\mu}(\hat{\mathbf{r}}) e^{-x(\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{r}}))} U(x, \delta\tilde{\mu}). \quad (\text{A17})$$

Integrating this equation gives

$$\begin{aligned} U(x, \delta\tilde{\mu}) &= 1 + \int_0^x dx' e^{x'(\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{r}}))} \delta\tilde{\mu} e^{-x'(\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{r}}))} U(x', \delta\tilde{\mu}) \\ &= 1 + \int_0^x dx' e^{x'(\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{r}}))} \delta\tilde{\mu} e^{-x'(\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{r}}))} \\ &\quad + \text{order}(\delta\tilde{\mu})^2, \end{aligned} \quad (\text{A18})$$

and so

$$\begin{aligned} e^{-\beta(\frac{\hat{p}^2}{2m} - \tilde{\mu} - \delta\tilde{\mu})} &= e^{-\beta(\frac{\hat{p}^2}{2m} - \tilde{\mu})} + \int_0^\beta dx' e^{(x' - \beta)(\frac{\hat{p}^2}{2m} - \tilde{\mu})} \delta\tilde{\mu} e^{-x'(\frac{\hat{p}^2}{2m} - \tilde{\mu})} \\ &\quad + \text{order}(\delta\tilde{\mu})^2. \end{aligned} \quad (\text{A19})$$

The derivative (A15) is then

$$\frac{\delta e^{-\beta(\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{r}}))}}{\beta\delta\tilde{\mu}(\mathbf{r})} \equiv \int_0^\beta dx' e^{(x' - \beta)(\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{r}}))} \delta(\hat{\mathbf{r}} - \mathbf{r}) e^{-x'(\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{r}}))}. \quad (\text{A20})$$

With these results, and again using the cyclic invariance of the trace, Eq. (A10) becomes

$$\left. -\frac{\delta\Omega^{(0)}(\beta | \tilde{\mu})}{\delta\tilde{\mu}(\mathbf{r})} \right|_\beta = \text{Tr}(e^{\beta(\frac{\hat{p}^2}{2m} - \tilde{\mu}(\hat{\mathbf{r}}))} + 1)^{-1} \delta(\hat{\mathbf{r}} - \mathbf{r}) = n(\mathbf{r}), \quad (\text{A21})$$

which is Eq. (27) of the text.

APPENDIX B: SCALING FROM UNITARY TRANSFORMATION

Define the one-parameter family of operators

$$\hat{U}(z) \equiv e^{\frac{z}{2\hbar}(\hat{\mathbf{q}} \cdot \hat{\mathbf{p}} + \hat{\mathbf{p}} \cdot \hat{\mathbf{q}})}, \quad (\text{B1})$$

and the related operators

$$\hat{X}(z) \equiv \hat{U}(z) \hat{\mathbf{q}} \hat{U}^{-1}(z), \quad \hat{Y}(z) \equiv \hat{U}(z) \hat{\mathbf{p}} \hat{U}^{-1}(z). \quad (\text{B2})$$

Then differentiation with respect to z

$$\frac{d\hat{X}(z)}{dz} = \hat{U}(z) \frac{i}{2\hbar} [(\hat{\mathbf{q}} \cdot \hat{\mathbf{p}} + \hat{\mathbf{p}} \cdot \hat{\mathbf{q}}), \hat{\mathbf{q}}] \hat{U}^{-1}(z) = \hat{X}(z), \quad (\text{B3})$$

$$\frac{d\hat{Y}(z)}{dz} = \hat{U}(z) \frac{i}{2\hbar} [(\hat{\mathbf{q}} \cdot \hat{\mathbf{p}} + \hat{\mathbf{p}} \cdot \hat{\mathbf{q}}), \hat{\mathbf{p}}] \hat{U}^{-1}(z) = -\hat{Y}(z), \quad (\text{B4})$$

gives [noting $\hat{X}(0) = \hat{\mathbf{q}}$, $\hat{Y}(0) = \hat{\mathbf{p}}$]

$$\begin{aligned} \hat{U}(z) \hat{\mathbf{q}} \hat{U}^{-1}(z) &= e^{z\hat{\mathbf{q}}}, & \hat{U}(z) \hat{\mathbf{p}} \hat{U}^{-1}(z) &= e^{-z\hat{\mathbf{p}}}, \\ & & -\infty < z < \infty. \end{aligned} \quad (\text{B5})$$

One more definition is needed:

$$\hat{U}_\gamma = \hat{U}[\ln(\gamma)] = e^{\frac{i}{2\hbar} \ln(\gamma) (\hat{\mathbf{q}} \cdot \hat{\mathbf{p}} + \hat{\mathbf{p}} \cdot \hat{\mathbf{q}})}. \quad (\text{B6})$$

This is the unitary operator that generates scale transformations

$$\hat{U}_\gamma A(\hat{\mathbf{q}}, \hat{\mathbf{p}}) \hat{U}_\gamma^{-1} = A(\gamma \hat{\mathbf{q}}, \gamma^{-1} \hat{\mathbf{p}}), \quad 0 < \gamma < \infty. \quad (\text{B7})$$

Now consider the density given by Eq. (27), insert unity $U_\gamma^{-1}U_\gamma = 1$, and use cyclic invariance of the trace

$$n(\mathbf{r}) = \text{Tr}\delta(\hat{\mathbf{q}} - \mathbf{r})\hat{\rho}_e = \text{Tr}U_\gamma^{-1}U_\gamma\delta(\hat{\mathbf{q}} - \mathbf{r})\rho = \text{Tr}\delta(\gamma\hat{\mathbf{q}} - \mathbf{r})\hat{\rho}_{e\gamma},$$

or

$$n_\gamma(\mathbf{r}) \equiv \gamma^3 n(\gamma\mathbf{r}) = \text{Tr}\delta(\hat{\mathbf{q}} - \mathbf{r})\hat{\rho}_{e\gamma}. \quad (\text{B8})$$

Here $\hat{\rho}_{e\gamma}$ is the transformed Fermi operator

$$\hat{\rho}_{e\gamma} \equiv U_\gamma\hat{\rho}_eU_\gamma^{-1} = (e^{\gamma^{-2}\beta[\frac{\hat{p}^2}{2m} - \gamma^2\tilde{\mu}^{(0)}(\gamma\hat{\mathbf{q}},\beta|n)]} + 1)^{-1}, \quad (\text{B9})$$

$$\hat{\rho}_{e\gamma} \equiv U_\gamma\hat{\rho}_e(\beta | n)U_\gamma^{-1} = \hat{\rho}_e(\gamma^{-2}\beta | n_\gamma). \quad (\text{B10})$$

The uniqueness of the functional $\tilde{\mu}^{(0)}(\hat{\mathbf{q}},\beta | n)$ gives the identification

$$\beta\tilde{\mu}(\gamma\hat{\mathbf{q}},\beta | n) = (\gamma^{-2}\beta)\tilde{\mu}(\hat{\mathbf{q}},\gamma^{-2}\beta | n_\gamma). \quad (\text{B11})$$

Consequently, the statistical operator $\hat{\rho}_e$ obeys the scaling relation

$$\hat{\rho}_{e\gamma}(\beta | n) = \hat{\rho}_e(\gamma^{-2}\beta | n_\gamma). \quad (\text{B12})$$

Confined systems can be represented by including a wall potential in the external potential. For example, spherically symmetric confinement is represented by $v_w = \Theta(R - \hat{q})\epsilon_w$, where ϵ_w is the potential barrier for escape from the volume $V = 4\pi R^3/3$, with the barrier taken arbitrarily large for the hard-wall limit. Under the scale transformation, the wall potential becomes

$$U_\gamma\Theta(R - \hat{q})U_\gamma^{-1} = \Theta(R - \gamma\hat{q}) = \Theta(\gamma^{-1}R - \hat{q}). \quad (\text{B13})$$

Thus the volume transforms as $V \rightarrow \gamma^{-3}V$.

Consider next the free energy functional (32)

$$\begin{aligned} F^{(0)}(\beta | n) &= \beta^{-1}\text{Tr}^{(1)}U_\gamma^{-1}U_\gamma[\dots] \\ &= \beta^{-1}\text{Tr}^{(1)}\left[(1 - \hat{\rho}_{e\gamma})\ln(1 - \hat{\rho}_{e\gamma}) + \hat{\rho}_{e\gamma}\ln\hat{\rho}_{e\gamma} \right. \\ &\quad \left. + \beta\gamma^{-2}\frac{\hat{p}^2}{2m}\hat{\rho}_{e\gamma}\right] \\ &= \gamma^{-2}F^{(0)}(\gamma^{-2}\beta | n_\gamma). \end{aligned} \quad (\text{B14})$$

The scaling for the energy density and entropy are found in a similar way

$$\begin{aligned} U^{(0)}(\beta | n) &= \gamma^{-2}U^{(0)}(\gamma^{-2}\beta | n_\gamma), \\ S^{(0)}(\beta | n) &= S^{(0)}(\gamma^{-2}\beta | n_\gamma). \end{aligned} \quad (\text{B15})$$

APPENDIX C: INEQUALITIES FROM SCALING

Equations (80) and (85) can be combined to give

$$\begin{aligned} (1 - \gamma^2)TS^{(0)}(\gamma^{-2}\beta | n_\gamma) &\leq F^{(0)}(\gamma^{-2}\beta | n_\gamma) - F^{(0)}(\beta | n_\gamma) \\ &\leq (1 - \gamma^2)TS^{(0)}(\beta | n_\gamma), \end{aligned} \quad (\text{C1})$$

and the application of the scaling laws gives

$$\begin{aligned} \frac{(1 - \gamma^2)}{\gamma^2}TS^{(0)}(\beta | n) &\leq [F^{(0)}(\beta | n) - F^{(0)}(\gamma^2\beta | n)] \\ &\leq \frac{(1 - \gamma^2)}{\gamma^2}TS^{(0)}(\gamma^2\beta | n). \end{aligned} \quad (\text{C2})$$

This implies

$$S^{(0)}(\beta | n) \leq S^{(0)}(\gamma^2\beta | n), \quad \gamma \leq 1, \quad (\text{C3})$$

or, equivalently,

$$S^{(0)}(\beta | n) \geq S^{(0)}(\beta | n_\lambda), \quad \gamma \geq 1. \quad (\text{C4})$$

Next, writing Eq. (80) in terms of the energy and density

$$\begin{aligned} U^{(0)}(\beta | n_\gamma) - U^{(0)}(\gamma^{-2}\beta | n_\gamma) \\ \leq T[S^{(0)}(\beta | n_\gamma) - S^{(0)}(\gamma^{-2}\beta | n_\gamma)], \end{aligned} \quad (\text{C5})$$

or with scaling

$$U^{(0)}(\beta | n_\gamma) - \gamma^2U^{(0)}(\beta | n) \leq T[S^{(0)}(\beta | n_\gamma) - S^{(0)}(\beta | n)]. \quad (\text{C6})$$

Then Eqs. (C3) and (C4) give

$$U^{(0)}(\beta | n_\gamma) \leq \gamma^2U^{(0)}(\beta | n), \quad \gamma \geq 1. \quad (\text{C7})$$

Expressing these results in terms of the same density by scaling gives the equivalent forms

$$U^{(0)}(\gamma^2\beta | n) \leq U^{(0)}(\beta | n), \quad \gamma \geq 1. \quad (\text{C8})$$

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