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Variational principle of classical density functional theory via Levy's constrained search methodWipsar Sunu Brams Dwandaru^{1,2} and Matthias Schmidt^{1,3}¹*H. H. Wills Physics Laboratory, University of Bristol, Royal Fort, Tyndall Avenue, Bristol BS8 1TL, United Kingdom*²*Jurusan Pendidikan Fisika, Universitas Negeri Yogyakarta, Bulaksumur, Yogyakarta, Indonesia*³*Theoretische Physik II, Physikalisches Institut, Universität Bayreuth, Universitätsstraße 30, D-95440 Bayreuth, Germany*

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We show that classical density functional theory can be based on the constrained search method [M. Levy, *Proc. Natl. Acad. Sci. USA* **73**, 6062 (1979)]. From the Gibbs inequality one first derives a variational principle for the grand potential as a functional of a trial many-body distribution. This functional is minimized in two stages. The first step consists of a constrained search of all many-body distributions that generate a given one-body density. The result can be split into internal and external contributions to the total grand potential. In contrast to the original approach by Mermin and Evans, here the intrinsic Helmholtz free-energy functional is defined by an explicit expression that does not refer to an external potential in order to generate the given one-body density. The second step consists of minimizing with respect to the one-body density. We show that this framework can be applied in a straightforward way to the canonical ensemble.

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I. INTRODUCTION

The variational principle of density functional theory (DFT) was originally formulated for ground-state properties of quantum systems by Hohenberg and Kohn in 1964 [1]. The extension to nonzero temperatures was performed by Mermin in the following year [2], here still formulated for quantum systems. The application to the statistical mechanics of classical systems, i.e., the development of classical DFT, was initiated about a decade later through the work of Ebner, Saam, and Stroud [3–5]. The generality of the framework was fully realized by Evans [6]. His 1979 article continues to be the standard reference on the subject; there are more recent review [7–9] and textbook [10] presentations.

The Hohenberg-Kohn theorem applies to one-particle density distributions that correspond to a particular external (one-body) potential v in the Hamiltonian, in which the kinetic and internal interaction are those of the true system [1,2]. One refers to v -representability of the one-particle density, i.e., the condition that a one-particle density is generated by some external potential v . However, it was realized, already in the original Hohenberg-Kohn paper, that v -representability is not guaranteed for an arbitrarily chosen density ρ [1,11,12]. One argues that this does not pose any problems in the practical applications of DFT to quantum systems [13]. In the development of the theory, it turned out that there indeed exist non- v -representable densities, i.e., one-body densities that are not associated to any ground-state wave function [14]. The original Hohenberg-Kohn theorem does not apply to these.

In 1979, Levy introduced an alternative foundation of DFT for quantum systems, based on a constrained, two-stage search [11]. Here a weaker condition, known as N -representability, is used, where the density distribution may be directly obtained from some antisymmetric N -body wave function, although an external potential that generates this wave function need not exist [11,14,15]. One defines exchange-correlation functional that demands searching all wave functions that return the fixed (trial) one-body density. The latter need not be v -representable. Subsequently, a method similar to Levy's was proposed by Lieb [16], called the generalized Legendre

transform [12]. Instead of searching all wave functions, the functional searches all possible external potentials that correspond to a fixed density. Kohn adopted the constrained search for his Nobel lecture [13], and it is viewed as an important theoretical contribution to the foundation of DFT for electronic structure. Practical applications of constrained search functionals are of ongoing research interest; see e.g., Refs. [12,17]. Levy gives a brief historic account of the development of his ideas in Ref. [18].

Given the significance of Levy's and Lieb's methods for electronic structure, it is somewhat surprising that there are very few studies that point to the use of these methods in classical systems. One example is the work by Weeks [19], where v -representability of the one-body density in some finite region of space is investigated through the Gibbs inequality. Although Weeks cites Levy's original paper [11] and makes a remark that his formulation is in spirit similar to that of Levy, it seems that his method is related more to Lieb's generalized Legendre transform method. Earlier work has been carried out in order to investigate the existence of an external potential that is associated to a given equilibrium one-body density [20]. It is concluded that there is such an external potential that produces any given density for any (classical) system without hard-core interaction. Although one might guess from general arguments that the constrained search can be applied to classical DFT, to the best of our knowledge, this procedure has not been spelled out explicitly in the literature.

In the present article we show how to formulate the variational principle of classical DFT based on Levy's constrained search method. This alternative can provide further insights into the foundation of classical DFT. In particular the intrinsic free-energy functional is defined here without implicit reference to an external potential v . A more relaxed condition for ρ , similar to that of N -representability, is imposed. Here, the one-body density is only required to be obtained from an arbitrarily chosen many-body probability distribution f . We refer to this condition as f -representability of a given ρ . While distinguishing between the different types of representability in practical DFT calculations seems unnecessary, we find

the discrimination to be very useful for conceptual purposes and hence point out throughout the manuscript which of the conventions is followed in the reasoning. We also show that Levy's method can be applied in a straightforward way to the canonical ensemble. There is considerable current interest in the theoretical description of the behavior of small systems, where the grand and the canonical ensembles are inequivalent in general, and the latter might model certain (experimental) realizations of strongly confined systems more closely. Several relatively recent contributions address the problem of formulating DFT in the canonical ensemble [21–26]. The authors of these papers consider the important problem of how to obtain DFT approximations that make computations in the canonical ensemble feasible. Our present article has a much lower goal: We are concerned only with formulating the variational principle in an alternative way.

This article is organized as follows. We start by defining the grand potential as a functional of the many-body probability distribution in Sec. II. This is a necessary step and our presentation follows [6–8,10]. In Sec. III we give a brief overview of the standard proof of DFT, expressing the free energy as a functional of the one-body density based on a one-to-one correspondence between the one-body density and the external potential. The full derivation is widely known and can be found in numerous references [6–8,10,27]. We proceed, in Sec. IV, by formulating the intrinsic free-energy functional via the constrained search method; our presentation is similar to Levy's original work [11]. Our central result is the definition (22) of the intrinsic free-energy functional, without reference to an external potential. We summarize the essence of Levy's argument as a double minimization [18] in Sec. V. In Sec. VI we apply this to the canonical ensemble and we conclude in Sec. VII.

II. GRAND POTENTIAL FUNCTIONAL OF THE MANY-BODY DISTRIBUTION

In the grand canonical ensemble of a system of classical particles, the equilibrium probability distribution for N particles at temperature T is assumed to exist and to be given by

$$f_0 = \Xi^{-1} \exp[-\beta(H_N - \mu N)], \quad (1)$$

where H_N is the Hamiltonian of N particles, μ is the chemical potential, and $\beta = 1/(k_B T)$, with k_B being the Boltzmann constant. The normalization constant is the grand canonical partition sum

$$\Xi = \text{Tr}_{\text{cl}} \exp[-\beta(H_N - \mu N)], \quad (2)$$

where Tr_{cl} represents the classical trace, i.e., the sum over total particle number and integral over all degrees of freedom

$$\text{Tr}_{\text{cl}} = \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int d\mathbf{r}_1 \dots d\mathbf{r}_N \int d\mathbf{p}_1 \dots d\mathbf{p}_N, \quad (3)$$

where h is the Planck constant, $\mathbf{r}_1, \dots, \mathbf{r}_N$ are the position coordinates, and $\mathbf{p}_1, \dots, \mathbf{p}_N$ are the momenta of particles 1, \dots , N .

One introduces the grand potential as a functional of the many-body probability distribution,

$$\Omega[f] = \text{Tr}_{\text{cl}} f (H_N - \mu N + \beta^{-1} \ln f), \quad (4)$$

where f is a variable trial probability distribution that satisfies the normalization condition

$$\text{Tr}_{\text{cl}} f = 1. \quad (5)$$

Note that f as an argument of functional (4) can be quite general and need not be linked to an external potential at this stage. Inserting the equilibrium probability distribution (1) into (4) one obtains

$$\begin{aligned} \Omega[f_0] &= \text{Tr}_{\text{cl}} f_0 (H_N - \mu N + \beta^{-1} \ln f_0) \\ &= \text{Tr}_{\text{cl}} f_0 (H_N - \mu N + \beta^{-1} [-\ln \Xi - \beta(H_N - \mu N)]) \\ &= -\beta^{-1} \ln \Xi \equiv \Omega_0, \end{aligned} \quad (6)$$

where Ω_0 is the equilibrium grand potential. An important property of functional (4) is that it satisfies the variational principle

$$\Omega[f] > \Omega[f_0], \quad f \neq f_0, \quad (7)$$

which may be proven using the Gibbs-Bogoliubov relation as follows. First, from Eqs. (1) and (6), $\Omega[f]$ of Eq. (4) can be written as

$$\Omega[f] = \Omega[f_0] + \beta^{-1} \text{Tr}_{\text{cl}} f \ln \left(\frac{f}{f_0} \right). \quad (8)$$

According to the Gibbs inequality [6,10],

$$f \ln \left(\frac{f_0}{f} \right) < f \left(\frac{f_0}{f} - 1 \right), \quad (9)$$

and hence

$$\text{Tr}_{\text{cl}} f \ln \left(\frac{f}{f_0} \right) > \text{Tr}_{\text{cl}} (f - f_0). \quad (10)$$

Since f and f_0 are normalized, i.e., satisfy (5), the right-hand side of the inequality above vanishes and

$$\beta^{-1} \text{Tr}_{\text{cl}} f \ln \left(\frac{f}{f_0} \right) > 0. \quad (11)$$

Thus the second term on the right-hand side of (8) is positive, and the inequality (7) follows.

For classical particles the Hamiltonian may be restricted to the form

$$H_N = \sum_{i=1}^N \frac{p_i^2}{2m} + U(\mathbf{r}_1, \dots, \mathbf{r}_N) + \sum_{i=1}^N v(\mathbf{r}_i), \quad (12)$$

where the first term is the total kinetic energy, with the squared momentum $p_i^2 = \mathbf{p}_i \cdot \mathbf{p}_i$ of the i -th particle, U is the interatomic potential between the particles, v is an (arbitrary) external one-body potential, and m is the particle mass. The equilibrium one-body density at position \mathbf{r} is given as a configurational average

$$\rho_0(\mathbf{r}) = \text{Tr}_{\text{cl}} f_0 \hat{\rho}(\mathbf{r}), \quad (13)$$

where the density operator for N particles is defined as

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i). \quad (14)$$

The functional form (4) was originally introduced by Mermin [2] for (finite-temperature) quantum systems, where the grand potential is a functional of a (trial) density matrix. The variational principle (7) will be used in Secs. III and IV below, where we present two alternative derivations of the intrinsic free energy as a functional of the one-body density.

2. MERMIN-EVANS DERIVATION OF THE FREE-ENERGY FUNCTIONAL

Evans gave a formal proof that the intrinsic free energy of a system of classical particles is a functional of the one-body density [7]. Here we briefly lay out his chain of arguments. The many-body distribution f_0 as given in (1) is a functional of the external potential v through Eq. (12), and therefore ρ_0 is a functional of v via (13). This, in principle, requires solution of the many-body problem and the dependence is in accordance with physical intuition, i.e., it is the action of v that generates the shape of the density profile ρ_0 .

However, the more useful result that can be deduced [7], is that once the interatomic interaction potential U is given, f_0 is a functional of ρ_0 . The proof of this statement rests on *reductio ad absurdum* [6,7,10], where for a given interaction potential U , v is uniquely determined by ρ_0 . The resultant v then determines f_0 via (1) and (12). Hence, f_0 is a functional of ρ_0 .

An important consequence in this reasoning is that for given interaction potential U ,

$$\mathcal{F}[\rho] = \text{Tr}_{\text{cl}} f_0 \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U + \beta^{-1} \ln f_0 \right) \quad (15)$$

is a unique functional of the (trial) one-body density ρ . Here, the dependence of f_0 on the external potential, v , is now implicit only through the one-body density, ρ . We will comment on this sequence of dependencies in the conclusions, after having laid out Levy's alternative method to define a free-energy functional in Sec. IV. Furthermore, using a Legendre transform, the grand potential functional is obtained for a given external potential as

$$\Omega_v[\rho] = \mathcal{F}[\rho] + \int d\mathbf{r} [v(\mathbf{r}) - \mu] \rho(\mathbf{r}). \quad (16)$$

The functional $\Omega_v[\rho]$ returns its minimum value if $\rho = \rho_0$, i.e., if the trial density is the true equilibrium one-body density of the system under the influence of v . The value is the grand potential Ω_0 . The existence of the minimum value of $\Omega_v[\rho]$ may be proven by considering another equilibrium density ρ' associated with a probability distribution f' of unit trace (5), such that

$$\begin{aligned} \Omega[f'] &= \text{Tr}_{\text{cl}} f' (H_N - \mu N + \beta^{-1} \ln f') \\ &= \mathcal{F}[\rho'] + \int d\mathbf{r} [v(\mathbf{r}) - \mu] \rho'(\mathbf{r}) \\ &= \Omega_v[\rho'], \end{aligned} \quad (17)$$

where

$$\mathcal{F}[\rho'] = \text{Tr}_{\text{cl}} f' \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U + \beta^{-1} \ln f' \right). \quad (18)$$

However, it is known from Eq. (7) that $\Omega[f'] > \Omega[f_0]$, for $f' \neq f_0$, thus it follows that

$$\Omega_v[\rho'] > \Omega_v[\rho_0]. \quad (19)$$

In other words, the correct equilibrium one-body density, ρ_0 , minimizes $\Omega_v[\rho]$ over all density functions that can be associated with a potential v .

This important result may be stated as a functional derivative

$$\left. \frac{\delta \Omega_v[\rho]}{\delta \rho(\mathbf{r})} \right|_{\rho_0} = 0 \quad (20)$$

and

$$\Omega_v[\rho_0] = \Omega_0. \quad (21)$$

To conclude, the formal argument for the definition (15) of the intrinsic free-energy functional, $\mathcal{F}[\rho]$, is based on v -representability of the one-body density. A v -representable ρ is one that is associated with a probability distribution, f , of the given Hamiltonian H_N with external potential v [11,13]. This condition was originally introduced for quantum systems and is implicit in the current approach. It is used to prove the chain of dependency outlined above (15) and confirmed for a large class of (classical) systems in Ref. [20].

5. IV. FREE-ENERGY FUNCTIONAL VIA LEVY'S CONSTRAINED SEARCH METHOD

Here we show how one may alternatively define a free-energy functional via Levy's method. This is based on the weaker condition of f -representability, where trial density fields ρ need not necessarily be associated with some external potential. We define the intrinsic Helmholtz free-energy functional as

$$\mathcal{F}_L[\rho] = \min_{f \rightarrow \rho} \left[\text{Tr}_{\text{cl}} f \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U + \beta^{-1} \ln f \right) \right], \quad (22)$$

where the minimization searches all probability distributions f , that are normalized according to (5), and that yield the fixed trial one-body density ρ via

$$\rho(\mathbf{r}) = \text{Tr}_{\text{cl}} f \hat{\rho}(\mathbf{r}). \quad (23)$$

The notation $f \rightarrow \rho$ in (22) indicates the relationship (23). Note that (i) in general there will be many different forms of f that yield the same ρ , and (ii) no further conditions on f are imposed, apart from its normalization. In particular, the form of f need not be of Boltzmann-type containing the interaction potential U (as was the case in Sec. III). Hence ρ need only be f -representable, but not necessarily v -representable. $\mathcal{F}_L[\rho]$ returns a minimum value by choosing the probability distribution that minimizes the term in brackets in (22). Note that the functional form of this term is formally equivalent to (15) and that it is a sum of contributions due to kinetic energy, internal interaction energy U , and (negative) entropy $k_B f \ln f$ multiplied by T .

The grand potential functional for a given external potential is then

$$\Omega_L[\rho] = \mathcal{F}_L[\rho] + \int d\mathbf{r} [v(\mathbf{r}) - \mu] \rho(\mathbf{r}). \quad (24)$$

This functional possesses two important properties. (i) At the equilibrium density it yields the equilibrium grand potential

$$\Omega_L[\rho_0] = \Omega_0, \quad (25)$$

where ρ_0 is given by (13) and Ω_0 by (6). This value also constitutes the minimum such that

$$\Omega_L[\rho] \geq \Omega_0. \quad (26)$$

In order to prove (25) and (26), we introduce additional notation. Let $f_{\min}^{\rho_0}$ be the probability distribution that satisfies the right-hand side of Eq. (22). Then it follows that

$$\mathcal{F}_L[\rho] = \text{Tr}_{\text{cl}} f_{\min}^{\rho} \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U + \beta^{-1} \ln f_{\min}^{\rho} \right), \quad (27)$$

and for the case of the equilibrium density,

$$\mathcal{F}_L[\rho_0] = \text{Tr}_{\text{cl}} f_{\min}^{\rho_0} \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U + \beta^{-1} \ln f_{\min}^{\rho_0} \right). \quad (28)$$

First, we proof the inequality (26). By its very definition (24), the left-hand side of (26) may be rearranged into

$$\begin{aligned} & \int d\mathbf{r} [v(\mathbf{r}) - \mu] \rho(\mathbf{r}) + \mathcal{F}_L[\rho] \\ &= \int d\mathbf{r} [v(\mathbf{r}) - \mu] \rho(\mathbf{r}) \\ & \quad + \text{Tr}_{\text{cl}} f_{\min}^{\rho} \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U + \beta^{-1} \ln f_{\min}^{\rho} \right) \\ &= \text{Tr}_{\text{cl}} f_{\min}^{\rho} (H_N - \mu N + \beta^{-1} \ln f_{\min}^{\rho}). \end{aligned} \quad (29)$$

But according to the inequality (7),

$$\text{Tr}_{\text{cl}} f_{\min}^{\rho} (H_N - \mu N + \beta^{-1} \ln f_{\min}^{\rho}) \geq \Omega_0. \quad (30)$$

Thus, combining (29) and (30), the inequality (26) is recovered. In order to prove (25), it is obvious from (7) that

$$\text{Tr}_{\text{cl}} f_{\min}^{\rho_0} (H_N - \mu N + \beta^{-1} \ln f_{\min}^{\rho_0}) \geq \Omega_0, \quad (31)$$

or, recalling (6),

$$\begin{aligned} & \text{Tr}_{\text{cl}} f_{\min}^{\rho_0} (H_N - \mu N + \beta^{-1} \ln f_{\min}^{\rho_0}) \\ & \geq \text{Tr}_{\text{cl}} f_0 (H_N - \mu N + \beta^{-1} \ln f_0). \end{aligned} \quad (32)$$

But $f_{\min}^{\rho_0}$ and f_0 generate the same one-body density ρ_0 , hence from

$$\begin{aligned} & \int d\mathbf{r} (v(\mathbf{r}) - \mu) \rho_0(\mathbf{r}) \\ & \quad + \text{Tr}_{\text{cl}} f_{\min}^{\rho_0} \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U + \beta^{-1} \ln f_{\min}^{\rho_0} \right) \\ & \geq \int d\mathbf{r} [v(\mathbf{r}) - \mu] \rho_0(\mathbf{r}) \\ & \quad + \text{Tr}_{\text{cl}} f_0 \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U + \beta^{-1} \ln f_0 \right), \end{aligned} \quad (33)$$

we obtain

$$\begin{aligned} & \text{Tr}_{\text{cl}} f_{\min}^{\rho_0} \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U + \beta^{-1} \ln f_{\min}^{\rho_0} \right) \\ & \geq \text{Tr}_{\text{cl}} f_0 \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U + \beta^{-1} \ln f_0 \right). \end{aligned} \quad (34)$$

However, by the very definition of $f_{\min}^{\rho_0}$, the following inequality should also hold:

$$\begin{aligned} & \text{Tr}_{\text{cl}} f_{\min}^{\rho_0} \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U + \beta^{-1} \ln f_{\min}^{\rho_0} \right) \\ & \leq \text{Tr}_{\text{cl}} f_0 \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U + \beta^{-1} \ln f_0 \right). \end{aligned} \quad (35)$$

The above two inequalities hold simultaneously, if and only if equality is attained,

$$\begin{aligned} & \text{Tr}_{\text{cl}} f_{\min}^{\rho_0} \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U + \beta^{-1} \ln f_{\min}^{\rho_0} \right) \\ &= \text{Tr}_{\text{cl}} f_0 \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U + \beta^{-1} \ln f_0 \right). \end{aligned} \quad (36)$$

Inserting (28) into (36) yields

$$\mathcal{F}_L[\rho_0] = \text{Tr}_{\text{cl}} f_0 \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U + \beta^{-1} \ln f_0 \right). \quad (37)$$

Furthermore, as

$$\begin{aligned} & \Omega_0 = \text{Tr}_{\text{cl}} f_0 (H_N - \mu N + \beta^{-1} \ln f_0) \\ &= \int d\mathbf{r} [v(\mathbf{r}) - \mu] \rho_0(\mathbf{r}) \\ & \quad + \text{Tr}_{\text{cl}} f_0 \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U + \beta^{-1} \ln f_0 \right), \end{aligned} \quad (38)$$

inserting (37) into (38) returns (25), which completes the proof. Equation (37) implies that if ρ is v -representable, then $\mathcal{F}_L[\rho] = \mathcal{F}[\rho]$. Moreover, $f_0 = f_{\min}^{\rho_0}$ means that f_0 may be obtained directly from ρ_0 even if v is unknown: Find the probability distribution that yields ρ_0 and which minimizes (22).

Finally, the inequality (26) implies that the functional derivative of the grand potential functional vanishes at equilibrium,

$$\left. \frac{\delta \Omega_L[\rho]}{\delta \rho(\mathbf{r})} \right|_{\rho_0} = 0. \quad (39)$$

For completeness we mention that it is convenient to split $\mathcal{F}_L[\rho]$ into two terms, viz. the ideal and exc's free-energy functionals, $\mathcal{F}_{\text{id}}[\rho]$ and $\mathcal{F}_{\text{exc}}[\rho]$, respectively, such that

$$\mathcal{F}_{\text{exc}}[\rho] \equiv \mathcal{F}_L[\rho] - \mathcal{F}_{\text{id}}[\rho], \quad (40)$$

where the free energy of the ideal gas (with no interaction potential present, $U = 0$) is given by

$$\mathcal{F}_{\text{id}}[\rho] = \beta^{-1} \int d\mathbf{r} \rho(\mathbf{r}) \{ \ln[\lambda^3 \rho(\mathbf{r})] - 1 \}, \quad (41)$$

where $\lambda = [\hbar^2 \beta / (4m\pi)]^{1/2}$. Thermodynamics enters by realizing that $\mathcal{F}_L[\rho_0]$ is the “intrinsic” Helmholtz free energy of the system such that the total free energy is the sum of internal and external contributions,

$$\mathcal{F}_L[\rho_0] + \int d\mathbf{r} \rho_0(\mathbf{r}) v(\mathbf{r}). \quad (42)$$

V. TWO-STAGE MINIMIZATION

The essence of the derivation presented in Sec. IV is a double minimization of the grand potential functional (4) of the many-body distribution. In the following, we spell this out more explicitly. From Sec. II we know that

$$\Omega_0 = \min_f \text{Tr}_{\text{cl}} f (H_N - \mu N + \beta^{-1} \ln f). \quad (43)$$

We decompose the right-hand side into a double minimization

$$\Omega_0 = \min_{\rho} \min_{f \rightarrow \rho} \text{Tr}_{\text{cl}} f (H_N - \mu N + \beta^{-1} \ln f), \quad (44)$$

where the inner minimization is a search under the constraint the f generates ρ [via relationship (23)]. For Hamiltonians of the form (12) the above can be written as

$$\begin{aligned} \Omega_0 = \min_{\rho} \min_{f \rightarrow \rho} \text{Tr}_{\text{cl}} f \\ \times \left[\sum_{i=1}^N \frac{p_i^2}{2m} + U + \sum_{i=1}^N v(\mathbf{r}_i) - \mu N + \beta^{-1} \ln f \right]. \end{aligned} \quad (45)$$

In the expression above

$$\text{Tr}_{\text{cl}} f \left[\sum_{i=1}^N v(\mathbf{r}_i) - \mu N \right] = \int d\mathbf{r} [v(\mathbf{r}) - \mu] \rho(\mathbf{r}), \quad (46)$$

because $f \rightarrow \rho$. So we may rewrite (45) as

$$\begin{aligned} \Omega_0 = \min_{\rho} \left\{ \int d\mathbf{r} [v(\mathbf{r}) - \mu] \rho(\mathbf{r}) \right. \\ \left. + \min_{f \rightarrow \rho} \text{Tr}_{\text{cl}} f \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U + \beta^{-1} \ln f \right) \right\} \end{aligned} \quad (47)$$

or

$$\Omega_0 = \min_{\rho} \left\{ \int d\mathbf{r} [v(\mathbf{r}) - \mu] \rho(\mathbf{r}) + \mathcal{F}_L[\rho] \right\}, \quad (48)$$

where $\mathcal{F}_L[\rho]$ is given by (22). Clearly (48) is equivalent to (25) and (26).

VI. DFT IN THE CANONICAL ENSEMBLE

One benefit of Levy’s method is that it allows straightforward generalization to the canonical ensemble, as we demonstrate in the following. In the canonical ensemble (i.e. for fixed number of particles, N) the equilibrium many-body distribution functions is

$$f_{N,0} = Z_0^{-1} \exp(-\beta H_N), \quad (49)$$

where the canonical partition sum is

$$Z_0 = \text{Tr}_N \exp(-\beta H_N), \quad (50)$$

with the canonical trace

$$\text{Tr}_N = \frac{1}{h^{3N} N!} \int d\mathbf{r}_1 \dots d\mathbf{r}_N \int d\mathbf{p}_1 \dots d\mathbf{p}_N. \quad (51)$$

In analogy to (4) we define the functional

$$F[f_N] = \text{Tr}_N f_N (H_N + \beta^{-1} \ln f_N), \quad (52)$$

where f_N is arbitrary N -body distribution that satisfies $\text{Tr}_N f_N = 1$. It is easy to show that the (total) Helmholtz free energy $F_0 = -\beta^{-1} \ln Z_0$ is obtained by inserting the equilibrium distribution (49) into the functional (52), hence

$$F_0 = F[f_{N,0}]. \quad (53)$$

Reasoning based on the Gibbs-Bogoliubov inequality, completely analogous to the arguments presented in Sec. II, yields

$$F_0 = \min_{f_N} F[f_N]. \quad (54)$$

We decompose this into a double minimization

$$F_0 = \min_{\rho_N} \min_{f_N \rightarrow \rho_N} F[f_N], \quad (55)$$

where the canonical one-body density distribution that is generated by f_N is

$$\rho_N(\mathbf{r}) = \text{Tr}_N f_N \hat{\rho}(\mathbf{r}), \quad (56)$$

with the density operator $\hat{\rho}(\mathbf{r})$ defined by (14). Clearly the density defined in this way satisfies $\int d\mathbf{r} \rho_N(\mathbf{r}) = N$, and there are no fluctuations in the total number of particles. For Hamiltonians of the form (12), Eq. (55) becomes

$$\begin{aligned} F_0 = \min_{\rho_N} \min_{f_N \rightarrow \rho_N} \text{Tr}_N f_N \\ \times \left[\sum_{i=1}^N \frac{p_i^2}{2m} + U + \sum_{i=1}^N v(\mathbf{r}_i) + \beta^{-1} \ln f_N \right]. \end{aligned} \quad (57)$$

In the above expression

$$\text{Tr}_N f_N \sum_{i=1}^N v(\mathbf{r}_i) = \int d\mathbf{r} v(\mathbf{r}) \rho_N(\mathbf{r}), \quad (58)$$

because $f_N \rightarrow \rho_N$ via (56). Hence

$$\begin{aligned} F_0 = \min_{\rho_N} \left[\int d\mathbf{r} v(\mathbf{r}) \rho_N(\mathbf{r}) + \min_{f_N \rightarrow \rho_N} \text{Tr}_N f_N \right. \\ \left. \times \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U + \beta^{-1} \ln f_N \right) \right], \end{aligned} \quad (59)$$

which we write as

$$F_0 = \min_{\rho_N} \left\{ \int d\mathbf{r} v(\mathbf{r}) \rho_N(\mathbf{r}) + F_N[\rho_N] \right\}, \quad (60)$$

where the intrinsic Helmholtz free-energy functional in the canonical ensemble is defined as

$$F_N[\rho_N] = \min_{f_N \rightarrow \rho_N} \text{Tr}_N f_N \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U + \beta^{-1} \ln f_N \right), \quad (61)$$

which is formally equivalent to the definition (22) of \mathcal{F}_L in the grand ensemble on identifying the different traces and different

types of many-body distributions. It is clear that the density distribution $\rho_{N,0}$ that minimizes the right-hand side of (60) is the true equilibrium distribution in the canonical ensemble

$$\rho_{N,0}(\mathbf{r}) = \text{Tr}_N f_{N,0} \hat{\rho}(\mathbf{r}) \quad (62)$$

and that $F_0 = F_N[\rho_{N,0}]$. The variational principle (60) implies that

$$\left. \frac{\delta F_N[\rho_N]}{\delta \rho_N(\mathbf{r})} \right|_{\rho_{N,0}} + v(\mathbf{r}) = 0, \quad (63)$$

where the derivative is taken under the constraint $\int d\mathbf{r} \rho_N(\mathbf{r}) = N$.

VII. DISCUSSION AND CONCLUSION

The formulation of DFT rests on the existence and uniqueness of the intrinsic free energy as a functional of the one-body density for a given classical system. We have described two methods for defining this quantity, via Eq. (15) based on the Mermin-Evans argument [2,7] and via (22) based on Levy's constrained search [11]. Following the derivations presented in Secs. III and IV, it is clear that these methods differ in their procedures and underlying principles.

In the Mermin-Evans sequence of arguments it is formally proven that the equilibrium many-body probability distribution, f_0 , is a functional of the equilibrium one-body density, ρ_0 . The existence of this functional rests on a sequence of functional dependencies. For given interatomic potential U and given one-body density ρ , there is a unique external potential v that generates this ρ . When input into the form of the many-body distribution in grand ensemble (1), this uniquely determines f_2 as used on the right-hand side of the definition (15) of the intrinsic free-energy functional $\mathcal{F}[\rho]$. This chain of dependency is implicit in order to properly define the free-energy functional via (15). Note that the naive view that the equilibrium probability distribution, f_0 , is a function of the external potential, v , such that (15) should also depend on v gives the impression that functional (15) is not independent of the external potential energy. Certainly this is not the case, as one may recall the argument above (15).

On the other hand, Levy's method does not rely on the above rather subtle argument. An appealing feature of the constrained

search method is the definition (22) of $\mathcal{F}_L[\rho]$. Here the intrinsic free-energy functional is explicitly independent of the external potential, which is not as easily observed from $\mathcal{F}[\rho]$ of Eq. (15). Kohn [13] and Levy [18] describe the constrained search method as a two-step minimization procedure, and we have laid out analogous reasoning in Sec. V.

The underlying principle of the Mermin-Evans method of defining the intrinsic free-energy functional is v -representability of the trial density, whereas Levy's functional is based on the weaker condition of f -representability. However, one may restrict the constrained search to the class of one-body densities that is v -representable. In this case Levy's functional (22) becomes equal to the Mermin-Evans functional (15). Hence, the constrained search method reduces to finding the equilibrium one-body density which correspond to an (equilibrium) external potential, v , that minimizes functional (24) over all one-body densities, ρ , each associated to a specific v . Furthermore, applying the Legendre transform on functional (24) and minimizing a set of external potentials that yields a fixed one-body density, gives Week's free-energy functional [19].

In practice, minimizing Levy's version of the free-energy functional (22) will certainly not be easier than solving the many-body problem itself. Hence, whether the definition (22) helps to construct approximations for grand-canonical free-energy functionals remains an open question. For the case of the canonical ensemble we point the reader to the very significant body of work that has been carried out to formulate a computational scheme that permits to capture the effects that arise due to the constraint of fixed number of particles [21–26]. While the generalization to equilibrium mixtures is straightforward, we expect the application of Levy's method to DFT for quenched-annealed mixtures [28–31] to constitute an interesting topic for future work.

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