

Necessary and sufficient conditions for the N -representability of density functionals

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It is well known that variational optimization of the energy using approximate density functionals can give results below the true ground-state energy. This can be attributed to the fact that many approximate density functionals are not N -representable. This paper presents a general method for deriving N -representability conditions in density-functional theory and presents specific results for the kinetic energy, the electron-electron interaction energy, the Hohenberg-Kohn functional, and the exchange-correlation energy functional. The method can be extended to energy densities, and specific results are presented for two different choices of the kinetic-energy density. Max-min variational principles for minimizing the energy subject to N -representability constraints are presented. Some constraints on exchange-correlation density functionals are among our secondary findings. In particular, we construct an exact meta-generalized-gradient-approximation (meta-GGA) functional using a Legendre transform and use this expression to show that (a) meta-GGAs should be convex functionals of the kinetic-energy density and (b) the sum of the Coulomb energy and the meta-GGA exchange-correlation energy should be a convex functional of the electron density.

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I. v - AND N -REPRESENTABILITY PROBLEMS IN DENSITY-FUNCTIONAL THEORY

Density-functional theory is based on two fundamental theorems [1–3]: (1) the electron density determines all the properties of an electronic system and (2) the exact ground-state electronic energy for N electrons bound in the external potential $v(\mathbf{r})$ can be determined by minimizing the energy functional with respect to all N -electron electron densities,

$$E_{g.s.}[v;N] = \min_{\langle\rho\rangle=N} E_v[\rho]. \quad (1)$$

The electron density (densities, if the ground state is degenerate) that achieves the minimum is the electron density of the ground state,

$$\rho_{g.s.}[v;N,\mathbf{r}] = \arg \min_{\langle\rho\rangle=N} E_v[\rho]. \quad (2)$$

These remarkable results are usually called the first and second Hohenberg-Kohn theorems, respectively [1]. The first Hohenberg-Kohn theorem allows one to conceive of a “density-functional theory,” in which the ground-state electron density replaces the electronic wave function as the fundamental descriptor of an electronic system [4–7]. How does one determine the ground-state electron density? The second Hohenberg-Kohn theorem is the variational principle that provides the basis for numerical computation of the ground-state electron density and the ground-state electronic energy.

At first density-functional theory seems too good to be true: the daunting complexity of the N -electron wave function (which depends on $3N$ spatial coordinates and N dichotomic spin variables) has been replaced by the electron density, a single three-dimensional function that is arguably even simpler than an orbital (since the electron density is never negative, while an orbital might be). But density-functional theory (DFT) is not as simple as it seems. First of all, the Hohenberg-Kohn theorems are mathematically

subtle. The “naive” proof of the Hohenberg-Kohn theorems holds only for electron densities that correspond to either (a) a ground-state electron density for some external potential [1] or (b) a weighted average of ground-state electron densities corresponding to that potential [3,8,9]. Such electron densities are said to be (a) pure-state v -representable or (b) ensemble v -representable. This would be fine if every electron density was ensemble v -representable; however, there is a dense subset of electron densities that is not v -representable at all [9]. (For example, every electron density that is zero in a finite volume of space is non- v -representable [9–13].) In order to use the variational principle, the energy functional $E_v[\rho]$ needs to be defined for every nonnegative electron density that is appropriately normalized; this is called the v -representability problem.

Resolving the v -representability problem required the efforts of an assortment of excellent mathematicians and mathematically inclined scientists [2,3,10,11,13,14]. At this stage the authors view the problem as solved, albeit perhaps not completely understood. At a purely mathematical level, the energy functional can be constructed in any of three different ways. The first, and most common, way is to reformulate density-functional theory in a way that does not require v -representability. Examples of this approach include the wave-function constrained search of Levy [2,15], the density-matrix constrained search of Valone [14], and the Legendre transform formulation of Lieb [3,16]. The second way avoids treating non- v -representable densities altogether by using the dual formulation of density-functional theory to rewrite the variational principle as an optimization with respect to external potentials [17]. The third way attacks the v -representability problem head on and seeks to extend the domain of the energy functional to non- v -representable densities by imposing constraints on the form of the functional (e.g., that the functional should be size consistent [18] and satisfy the variational principle) [13].

Unfortunately, none of these approaches to the energy functional is computationally practical, since the expense of computational schemes based on the exact energy functional is typically several times greater than solving the Schrödinger equation directly [19]. Practical applications of density-functional theory require approximating the density functional for the energy.

Given an approximate energy functional $\tilde{E}_v[\rho]$, the variational principle is no longer valid. That is, minimizing an *approximate* energy functional can sometimes give results below the true energy. (There are a few approximate energy functionals that are rigorous upper bounds to the true energy; unfortunately these functionals do not seem to be very accurate [3,20].) The fact that most approximate energy functionals sometimes give results below the true ground-state energy is called the *N-representability problem* in density-functional theory [21–26].

The *N-representability problem* seems to be a feature of any method that uses a reduced description of an electronic system, instead of the full *N*-electron wave function. The *N-representability problem* was first noticed in the context of the theory of reduced density matrices; naive minimization of the energy with respect to the two-electron reduced density matrix

$$E_v[\Gamma_2] = \int \int \int \int \left[\delta(\mathbf{r}_1 - \mathbf{r}'_1) \delta(\mathbf{r}_2 - \mathbf{r}'_2) \right. \\ \left. \times \left(\frac{-\nabla_1^2 + -\nabla_2^2}{2(N-1)} + \frac{v(\mathbf{r}_1) + v(\mathbf{r}_2)}{N-1} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \right. \\ \left. \times \Gamma_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) \right] d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}'_1 d\mathbf{r}'_2 \quad (3)$$

gives a result far below the true ground-state energy. The reason is that one must restrict the variational principle to the subset of reduced density matrices that correspond to *N*-electron systems. That is, the domain of the variational principle is restricted to Γ_2 , which can be written in the following form:

$$\Gamma_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) = \frac{N(N-1)}{2} \sum_i p_i \langle \Psi_i(\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}_3, \dots, \mathbf{r}_N) \\ \times |\Psi_i(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)\rangle_{3, \dots, N} \quad (4)$$

where the Ψ_i are appropriately antisymmetric fermionic wave functions and the p_i represent the probability of observing each wave function in the ensemble. Though there has been a lot of recent work on the approach based on the two-electron density matrix [27–35], progress is hampered by the lack of efficient algorithms and the fact that it is practically impossible to exactly enforce the exact *N-representability* constraints.

In order to draw the link to density-functional theory, it is helpful to consider an alternative to the usual variational principle in terms of the two-electron density matrix. Instead of minimizing the energy functional in Eq. (3) on the domain of *N-representable* Γ_2 , one designs a new functional $E_v^{(N\text{-rep})}[\Gamma_2]$ that can be minimized over *all* Γ_2 , without re-

striction [36,37]. As for the functionals in density-functional theory, there is no practical way to construct $E_v^{(N\text{-rep})}[\Gamma_2]$. Energy minimization of approximations to this functional will sometimes produce energies that are below the true energy. In this way the *N-representability problem* for Γ_2 is equivalent to an *N-representability problem* for the energy functional.

People sometimes erroneously state that there is no *N-representability problem* in density-functional theory. It is true that there is no *N-representability problem* for the electron density: every nonnegative function that is normalized to the number of electrons, *N*, is an *N-representable* electron density [38–40], so it is easy to restrict the variational principle for the energy to *N-representable* electron densities. It is much harder to design approximate energy functionals that are accurate upper bounds to the true ground-state energy. It can be said, then, that the *N-representability problem* in density-functional theory is not related to *N-representability* of the electron density but, instead, to the *N-representability* of the approximate functionals that are used to evaluate the energy [21–25].

One can envision treating the electronic structure problem using variables that are intermediate in complexity between the electron density (simple *N-representability* constraints; difficult approximation problem for the energy functional) and the two-electron reduced density matrix (difficult *N-representability* constraints; simple and explicit energy functional). For example, there has been a lot of recent interest in using the electron pair distribution function, or 2-density, as the fundamental descriptor for Coulomb systems [37,41–53]. (For the 2-density, presumably both the functional-approximation problem and the *N-representability problem* are of “medium” difficulty.) While studying the *N-representability problem* for the 2-density [54], We realized that the same techniques might be useful in density-functional theory. This paper is the result of those investigations.

In the next section of this paper, necessary and sufficient conditions for the *N-representability* of the Hohenberg-Kohn functional, the kinetic-energy functional, the electron-electron interaction energy functional, and the exchange-correlation energy functional are presented. Section III shows how *N-representability* constraints can inform the construction of energy densities, especially the kinetic-energy density. We conclude with a brief summary of our main results.

II. N-REPRESENTABILITY OF DENSITY FUNCTIONALS

A. The Hohenberg-Kohn functional

It is useful to partition the energy in density-functional theory into the term that can be explicitly computed, $\langle \rho v \rangle$, and the term that must be approximated, $F[\rho]$,

$$E_v[\rho] = F[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r}. \quad (5)$$

$F[\rho]$ is called the Hohenberg-Kohn functional; the Hohenberg-Kohn functional is equal to the sum of the kinetic

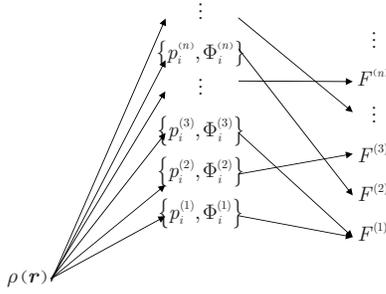


FIG. 1. A pictorial depiction of the N -representability problem for functionals. Any given electron density corresponds to a large number of potential N -fermion states, as shown in the first two columns. These N -fermion states, in turn, map onto the N -representable values for the functional. In this schematic representation, any value of F that does not appear in the third column is not N -representable.

energy $T[\rho]$ and the electron-electron repulsion energy $V_{ee}[\rho]$.

The N -representability problem arises when one wishes to approximate $F[\rho]$. For every electron density that is nonnegative and normalized to the number of electrons, N , there are an infinite number of possible N -electron precursor states,

$$\rho(\mathbf{r}_1) = N \sum_i p_i \langle \Psi_i(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) | \Psi_i(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \rangle_{2, \dots, N}. \quad (6)$$

Each of these states is associated with a possible choice of $F[\rho]$,

$$F[\{p_i, \Psi_i\}] = \sum_i p_i \langle \Psi_i | \hat{T} + V_{ee} | \Psi_i \rangle. \quad (7)$$

Definition of N -representable functionals [22]. An approximate functional $\tilde{F}[\rho]$ is said to be N -representable if and only if for every electron density $\tilde{\rho}(\mathbf{r})$ there exists some N -electron state $\{\tilde{p}_i, \tilde{\Psi}_i\}$ that (i) is associated with this electron density via Eq. (6) and (ii) is associated with the value of the functional $\tilde{F}[\tilde{\rho}] = F[\{\tilde{p}_i, \tilde{\Psi}_i\}]$ via Eq. (7).

The meaning of this definition is elucidated in Fig. 1. Any reasonable electron density will correspond to a huge number of possible N -fermion states $\{p_i, \Psi_i\}$. The value of $\tilde{F}[\tilde{\rho}]$ should also correspond to one of these states. Otherwise the definition of the functional would not be physically reasonable because there would not exist any N -fermion state that has the density $\tilde{\rho}(\mathbf{r})$ and the expectation value $\tilde{F}[\tilde{\rho}]$.

Note that an approximate functional could be N -representable and still be extremely inaccurate. N -representability conditions are necessary conditions for accurate functionals because N -representable functionals will never give energies below the true ground-state energy. However, it is possible for a functional to be N -representable and still give energies far above the true ground-state energy. The N -representability of a functional is not sufficient to ensure its accuracy. In fact, it follows from the constrained

search procedure that the exact Hohenberg-Kohn functional is the smallest N -representable functional [13,14,36],

$$F[\rho] = \min_{\{p_i, \Psi_i\} \rightarrow \rho(\mathbf{r})} F[\{p_i, \Psi_i\}]. \quad (8)$$

The N -representability constraints for the Hohenberg-Kohn functional can be derived by considering the energy to be a bifunctional of F and $\rho(\mathbf{r})$,

$$E_v[\rho; F] = F + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r}. \quad (9)$$

The energy is a linear function of F and a linear functional of $\rho(\mathbf{r})$.

The set of N -representable choices for F and $\rho(\mathbf{r})$ is closed and convex. That is, if $F^{(a)}$ and $\rho^{(a)}(\mathbf{r})$ are N -representable and $F^{(b)}$ and $\rho^{(b)}(\mathbf{r})$ are also N -representable, then any weighted average of these quantities is also N -representable. This is established by using the N -fermion state that corresponds to $F^{(a)}$ and $\rho^{(a)}(\mathbf{r})$ and the N -fermion state that corresponds to $F^{(b)}$ and $\rho^{(b)}(\mathbf{r})$ to construct a suitable representation for their weighted average. That is, for any $0 \leq t \leq 1$,

$$tF^{(a)} + (1-t)F^{(b)} = \sum_i \left\{ t [p_i^{(a)} \langle \Psi_i^{(a)} | \hat{T} + V_{ee} | \Psi_i^{(a)} \rangle + (1-t) [p_i^{(b)} \langle \Psi_i^{(b)} | \hat{T} + V_{ee} | \Psi_i^{(b)} \rangle] \right\}. \quad (10)$$

$$t\rho^{(a)}(\mathbf{r}_1) + (1-t)\rho^{(b)}(\mathbf{r}_1) = N \sum_i \left\{ t [p_i^{(a)} \langle \Psi_i^{(a)} | \Psi_i^{(a)} \rangle_{2,3,\dots,N}] + (1-t) [p_i^{(b)} \langle \Psi_i^{(b)} | \Psi_i^{(b)} \rangle_{2,3,\dots,N}] \right\}. \quad (11)$$

All of the key results on N -representability are simple consequences of the convexity of the N -representable set and the linearity of the energy functional. In particular, we have the following theorems.

Theorem 1: Necessary and sufficient conditions for N -representable $F[\rho]$. An approximate functional $\tilde{F}[\rho]$ is N -representable if and only if

$$\tilde{F}[\rho] + \int \rho(\mathbf{r})w(\mathbf{r})d\mathbf{r} \geq E_{g.s.}[w; N] \quad (12)$$

for every electron density $\rho(\mathbf{r})$ and every external potential $w(\mathbf{r})$.

Theorem 2: Max-Min variational principle for the ground-state energy. The exact N -electron ground-state energy can be determined by the max-min principle,

$$E_{g.s.}[v; N] = \max_{w(\mathbf{r})} \min_{\{\tilde{F}, \tilde{\rho} | \tilde{F} + \langle \tilde{\rho} w \rangle \geq E_{g.s.}[w; N]\}} \tilde{F} + \int \tilde{\rho}(\mathbf{r})v(\mathbf{r})d\mathbf{r} \quad (13)$$

Proofs. The ground-state energy can be determined by minimizing the energy expression over all N -fermion states,

$$E_{g.s.}[w;N] = \min_{\{p_i, \Psi_i\}} \sum_i p_i \langle \Psi_i | \hat{T} + V_{ee} + \sum_i w(\mathbf{r}_i) | \Psi_i \rangle. \quad (14)$$

Consequently, if $\tilde{F} + \langle \rho w \rangle$ is smaller than $E_{g.s.}[w;N]$, then it must be that $\tilde{F}[\rho]$ is not N -representable. This proves the “only if” part of Theorem 1 and establishes Eq. (12) as a necessary condition for N -representability.

Suppose that $\tilde{F}[\rho]$ is not N -representable. Then there exists some electron density $\tilde{\rho}(\mathbf{r})$ for which $\tilde{F}[\tilde{\rho}]$ does not correspond to any N -fermion state. This means that the pair $(\tilde{F}, \tilde{\rho}(\mathbf{r}))$ is outside the set of N -representable choices for F and $\rho(\mathbf{r})$. Because the set of N -representable $(F, \rho(\mathbf{r}))$ is convex, there must be a hyperplane so that the set of N -representable $(F, \rho(\mathbf{r}))$ is on one side of the hyperplane and the non- N -representable $(\tilde{F}, \tilde{\rho}(\mathbf{r}))$ is on the other side of the hyperplane [55,56]. That is, there exists an element of the dual space $(k, w(\mathbf{r}))$ such that

$$kF + \int \rho(\mathbf{r})w(\mathbf{r})d\mathbf{r} > k\tilde{F} + \int \tilde{\rho}(\mathbf{r})w(\mathbf{r})d\mathbf{r} \quad (15)$$

for all N -representable $(F, \rho(\mathbf{r}))$. The tightest inequality is obtained by selecting the N -representable $(F, \rho(\mathbf{r}))$ that minimizes the left-hand side of Eq. (15). This can be found using the variational principle:

$$\begin{aligned} & \min_{N\text{-representable } (F, \rho(\mathbf{r}))} \left(kF + \int \rho(\mathbf{r})w(\mathbf{r})d\mathbf{r} \right) \\ & \geq \min_{\{p_i, \Psi_i\}} \sum_i p_i \langle \Psi_i | k(\hat{T} + V_{ee}) + \sum_i w(\mathbf{r}_i) | \Psi_i \rangle \\ & > k\tilde{F} + \int \tilde{\rho}(\mathbf{r})w(\mathbf{r})d\mathbf{r}. \end{aligned} \quad (16)$$

Equation (15) is only meaningful if the left-hand side is greater than minus infinity, so it must be that $k > 0$. Dividing both sides of the equation by k gives

$$\begin{aligned} & \min_{\{p_i, \Psi_i\}} \sum_i p_i \left\langle \Psi_i \left| \hat{T} + V_{ee} + \sum_i \left(\frac{1}{k} w(\mathbf{r}_i) \right) \right| \Psi_i \right\rangle \\ & = E_{g.s.} \left[\frac{1}{k} w; N \right] > \tilde{F} + \int \tilde{\rho}(\mathbf{r}) \left(\frac{1}{k} w(\mathbf{r}) \right) d\mathbf{r}. \end{aligned} \quad (17)$$

Thus, if $\tilde{F}[\rho]$ is not N -representable, then there always exists some system [e.g., the N -electron system with $v(\mathbf{r}) = (1/k)w(\mathbf{r})$] for which $\tilde{F}[\tilde{\rho}] + \langle \tilde{\rho}v \rangle$ is less than the true N -electron ground-state energy. This establishes the “if” part of Theorem 1. Forcing Eq. (12) for every choice of $w(\mathbf{r})$ is sufficient for N -representability.

For any potential $w(\mathbf{r})$, Eq. (12) provides a necessary condition for N -representability. Minimizing the energy subject to this necessary condition gives a lower bound on the true energy,

$$E_{g.s.}[v;N] \geq \min_{\{\tilde{F}, \tilde{\rho} | \tilde{F} + \langle \tilde{\rho}v \rangle \geq E_{g.s.}[w;N]\}} \tilde{F} + \int \tilde{\rho}(\mathbf{r})v(\mathbf{r})d\mathbf{r}. \quad (18)$$

It is desirable for this bound to be as tight as possible; this is achieved by maximizing with respect to the constraint potential, as in Eq. (13). The resulting max-min principle always gives the correct ground-state energy because if $w(\mathbf{r})$ is chosen to be equal to $v(\mathbf{r})$, the exact ground-state energy is attained. ■

This proof [cf. Eq. (15)] relies on the dual space to the space, $(F, \rho(\mathbf{r}))$, where F is a real number and $\rho(\mathbf{r})$ is an electron density. The dual space to $(F, \rho(\mathbf{r}))$ is the set of bounded linear functionals on $(F, \rho(\mathbf{r}))$ [55]; that is, the dual space is defined as the set of all $(k, w(\mathbf{r}))$ such that

$$\left| kF + \int \rho(\mathbf{r})w(\mathbf{r})d\mathbf{r} \right| < \infty. \quad (19)$$

In this case, k can be any real number. The dual space to the space of possible electron densities is the space of external potentials $w(\mathbf{r})$ [3,17]. The space of external potentials always includes the space of essentially bounded functions $L^\infty(\mathbb{R}^3)$. However, depending on the amount of smoothness one requires from the electron density (which must be normalized, but one can impose additional constraints on its asymptotic decay or its differentiability), the space of external potentials may expand to include additional functions (like the potentials due to point charges) also [3,12].

B. The kinetic and electron-electron repulsion energy functionals

Establishing the N -representability of the Hohenberg-Kohn functional is extremely difficult, since it requires solving for the N -electron ground-state energy. However, the Hohenberg-Kohn functional is rarely modeled directly. Instead, one models the kinetic-energy and electron-electron repulsion energy functionals separately and adds the functionals together to construct the Hohenberg-Kohn functional,

$$F[\rho] = T[\rho] + V_{ee}[\rho]. \quad (20)$$

The N -representability conditions for these component functionals can also be deduced. The next two theorems are analogous to Theorem 1.

Theorem 3: Necessary and sufficient conditions for N -representable $V_{ee}[\rho]$. An approximate electron-electron repulsion energy functional $\tilde{V}_{ee}[\rho]$ is N -representable if and only if

$$\tilde{V}_{ee}[\rho] + \int \rho(\mathbf{r})w(\mathbf{r})d\mathbf{r} \geq E_{cl}[w;N] \quad (21)$$

for every electron density $\rho(\mathbf{r})$ and every external potential $w(\mathbf{r})$. Here $E_{cl}[w;N]$ is the ground-state energy of the classical electronic structure problem,

$$\begin{aligned}
E_{cl}[w;N] &= \min_{\{p_i, \Psi_i\}} \sum_i p_i \left\langle \Psi_i \left| \sum_i (\mathbf{r}_i) + V_{ee} \right| \Psi_i \right\rangle \\
&= \min_{r_i} \sum_i \left(w(\mathbf{r}_i) + \sum_{j>i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right). \quad (22)
\end{aligned}$$

Theorem 4: Necessary and sufficient conditions for N -representable $T[\rho]$. An approximate functional $\tilde{T}[\rho]$ is N -representable if and only if

$$\tilde{T}[\rho] + \int \rho(\mathbf{r})w(\mathbf{r})d\mathbf{r} \geq E_s[w;N] \quad (23)$$

for every electron density and every external potential $w(\mathbf{r})$. Here $E_s[w;N]$ is the ground-state energy of the noninteracting reference system,

$$E_s[w;N] = \min_{\{p_i, \Psi_i\}} \sum_i p_i \left\langle \Psi_i \left| \hat{T} + \sum_i w(\mathbf{r}_i) \right| \Psi_i \right\rangle. \quad (24)$$

Proofs. The proofs of Theorems 3 and 4 are very similar to each other and also to that of Theorem 1. Since the proof of Theorem 3 is especially similar to the proofs in Ref. [54], only the proof of Theorem 4 will be presented here.

The “only if” part of Theorem 4 follows directly the definition of the energy of the noninteracting system in Eq. (24).

Suppose that $\tilde{T}[\rho]$ is not N -representable. Then for some electron density $\tilde{\rho}(\mathbf{r})$ there exists no N -fermion system that has the electron density $\tilde{\rho}(\mathbf{r})$ and the kinetic energy $\tilde{T}[\tilde{\rho}]$. That is, if the functional $\tilde{T}[\rho]$ is not N -representable, then there must be some $(\tilde{T}, \tilde{\rho}(\mathbf{r}))$ that is not N -representable. Repeating the argument in Eqs. (10) and (11), the set of N -representable choices for T and $\rho(\mathbf{r})$ is a convex set. This means that there exists a hyperplane that separates the N -representable choices for $(T, \rho(\mathbf{r}))$ from the non- N -representable $(\tilde{T}, \tilde{\rho}(\mathbf{r}))$. Thus there exists a choice of $(k, w(\mathbf{r}))$ such that the inequality

$$kT + \int \rho(\mathbf{r})w(\mathbf{r})d\mathbf{r} \geq k\tilde{T} + \int \tilde{\rho}(\mathbf{r})w(\mathbf{r})d\mathbf{r} \quad (25)$$

is satisfied for every possible N -representable $(T, \rho(\mathbf{r}))$. The tightest bound on the N -representable set is achieved by minimizing over the set of N -representable $(T, \rho(\mathbf{r}))$, giving

$$\min_{\{p_i, \Psi_i\}} \sum_i p_i \left\langle \Psi_i \left| k\hat{T} + \sum_i w(\mathbf{r}_i) \right| \Psi_i \right\rangle > k\tilde{T} + \int \tilde{\rho}(\mathbf{r})w(\mathbf{r})d\mathbf{r}. \quad (26)$$

Since k must be positive (otherwise the left-hand side is minus infinity), dividing both sides by k gives

$$E_s\left[\frac{1}{k}w;N\right] > \tilde{T} + \int \tilde{\rho}(\mathbf{r})\left(\frac{1}{k}w(\mathbf{r})\right)d\mathbf{r}. \quad (27)$$

This establishes that if $\tilde{T}[\rho]$ is not N -representable, there will always exist a noninteracting system [specifically, the system with N electrons bound by the external potential $(1/k)w(\mathbf{r})$] for which the approximate ground-state energy is less than the true ground-state energy. ■

Theorems 3 and 4 have an interesting interpretation. Theorem 4 indicates that the N -representable kinetic-energy functionals are always be greater than or equal to the noninteracting kinetic-energy functional,

$$T_s[\rho] = \sup_{w(\mathbf{r})} \left(E_s[w;N] - \int \rho(\mathbf{r})w(\mathbf{r})d\mathbf{r} \right). \quad (28)$$

The kinetic energy of a system of interacting electrons is typically less than (and not equal to) the noninteracting kinetic energy, and so a correction for electron correlation is necessary,

$$T_c[\rho] = T_{exact}[\rho] - T_s[\rho] \geq 0. \quad (29)$$

This correction arises in a subtle way. The variational principle can be written in terms of the kinetic-energy functional and the electron-electron repulsion energy functional,

$$\min_{\{\rho\}=N} \left(T[\rho] + V_{ee}[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \right). \quad (30)$$

If $T[\rho]$ and $V_{ee}[\rho]$ are N -representable, then there exist N -fermion systems that are consistent with these functionals. However, it might be impossible to choose an N -fermion system that is consistent with both functionals at the same time. It is not enough to merely require that the functionals are N -representable; one can obtain energies below the true ground-state energy even if $T[\rho]$ and $V_{ee}[\rho]$ are both N -representable. One is guaranteed to have an upper bound on the total energy only if $T[\rho]$ and $V_{ee}[\rho]$ are *mutually* N -representable. That is, in order to guarantee that the result of the variational procedure Eq. (30) is greater than or equal to the true ground-state energy, one needs for $T[\rho]$ and $V_{ee}[\rho]$ to be representable by the same ensemble average of N -electron states.

Nonetheless, the N -representability constraints provide rigorous lower bounds to the true functionals. Since one can obtain energies below the true ground-state energy even with N -representable functionals, it would seem to be very prudent to impose the N -representability conditions: N -representability conditions will at least keep the results from getting “too bad.” This is probably one reason why the Kohn-Sham approach to density-functional theory is so effective: the Kohn-Sham approach effectively forces the kinetic-energy functional to be N -representable and helps prevent the “variational catastrophe” that often afflicts orbital-free implementations of density-functional theory.

Analogous to the max-min principle in Theorem 2, there are max-min variational principles for the ground-state energy in terms of the kinetic energy and the electron-electron repulsion energy. An example is Theorem 5.

Theorem 5: Max-min variational principle for the ground-state energy. The exact N -electron ground-state energy can be determined by the max-min principle,

$$\begin{aligned}
E_{g.s.}[v;N] &= \max_{w(\mathbf{r})} \min_{\{\tilde{T}, \tilde{\rho} | \tilde{T} + \int \tilde{\rho}(\mathbf{r})v(\mathbf{r})d\mathbf{r} \geq E_s[w;N]\}} \left(\tilde{T} + \int \tilde{\rho}(\mathbf{r})v(\mathbf{r})d\mathbf{r} + T_c[\tilde{\rho}] \right. \\
&\quad \left. + V_{ee}[\tilde{\rho}] \right), \quad (31)
\end{aligned}$$

$$E_{g.s.}[v;N] = \max_{w(\mathbf{r})} \min_{\{\tilde{T}, \tilde{\rho} | \tilde{T} + \langle \tilde{\rho} w \rangle \geq E_s[w;N]\}} \left(\tilde{T} + \int \tilde{\rho}(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + J[\tilde{\rho}] + E_{xc}[\tilde{\rho}] \right). \quad (32)$$

Here it is understood that $T_c[\rho]$ and $V_{ee}[\rho]$ are the exact functionals for the correlation kinetic energy [cf. (29)] and the electron-electron repulsion energy. The second equation rewrites this variational principle using the Coulomb energy ($J[\rho]$) and the exchange-correlation energy ($E_{xc}[\rho]$). It is assumed that $T_c[\rho] + V_{ee}[\rho] = J[\rho] + E_{xc}[\rho]$ is a convex functional. (If this is not true, the max-min procedure gives a lower bound on the ground-state energy.)

Proof. Requiring that Eq. (23) hold is a necessary condition for N -representability; this means that a lower bound to the ground-state energy is attained using just the inner minimization:

$$E_{g.s.}[v;N] \geq \min_{\{\tilde{T}, \tilde{\rho} | \tilde{T} + \langle \tilde{\rho} w \rangle \geq E_s[w;N]\}} \left(\tilde{T} + \int \tilde{\rho}(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + J[\tilde{\rho}] + E_{xc}[\tilde{\rho}] \right). \quad (33)$$

Clearly the tightest possible lower bound will be achieved by maximizing over all values of the constraint potential $w(\mathbf{r})$, so

$$E_{g.s.}[v;N] \geq \sup_{w(\mathbf{r})} \min_{\{\tilde{T}, \tilde{\rho} | \tilde{T} + \langle \tilde{\rho} w \rangle \geq E_s[w;N]\}} \left(\tilde{T} + \int \tilde{\rho}(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + J[\tilde{\rho}] + E_{xc}[\tilde{\rho}] \right). \quad (34)$$

It is less obvious that there exists a choice of constraining potential for which the equality is attained. The existence of such a value can be proved using the methods in Ref. [54]. Because $J[\rho] + E_{xc}[\rho]$ is convex by assumption, the energy expression

$$E_v[\rho;T] = T + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[\rho] \quad (35)$$

is also a convex functional of $\rho(\mathbf{r})$. This implies that the set of possible kinetic energies and electron densities for which the energy is less than the true ground-state energy is a convex set,

$$\mathcal{L}[v;N] = \{T, \rho | E_v[\rho;T] < E_{g.s.}[v;N]\}.$$

This convex set is a subset of the set of non- N -representable $(T, \rho(\mathbf{r}))$. However, the non- N -representable $(T, \rho(\mathbf{r}))$ that are not in $\mathcal{L}[v;N]$ have energies greater than or equal to the true ground-state energy, so they can be included in the variational procedure. Thus, if we could somehow construct a variational procedure that would never include any element of $\mathcal{L}[v;N]$, then we would find the ground-state energy,

$$E_{g.s.}[v;N] \geq \min_{\{\tilde{T}, \tilde{\rho} | \tilde{T}, \tilde{\rho} \in \mathcal{L}[v;N]\}} (E_v[\tilde{\rho};\tilde{T}]). \quad (36)$$

The set of N -representable $(T, \rho(\mathbf{r}))$ is also a convex set, $\mathcal{M}[N]$. Since every N -representable choice for the value of the kinetic energy gives an energy greater than or equal to the true ground-state energy, the sets $\mathcal{M}[N]$ and $\mathcal{L}[v;N]$ do not intersect. When two convex sets do not intersect, there is always a hyperplane that separates them. Thus, there exists a choice of $k > 0$ and $w(\mathbf{r})$ such that

$$kT + \int \rho(\mathbf{r}) w(\mathbf{r}) d\mathbf{r} \geq \alpha, \quad \{T, \rho(\mathbf{r})\} \in \mathcal{M}[N], \quad (37)$$

for every N -representable $\{T, \rho(\mathbf{r})\}$ and

$$\alpha > k\tilde{T} + \int \tilde{\rho}(\mathbf{r}) w(\mathbf{r}) d\mathbf{r}, \quad \{\tilde{T}, \tilde{\rho}(\mathbf{r})\} \in \mathcal{L}[v;N], \quad (38)$$

for every $\{\tilde{T}, \tilde{\rho}(\mathbf{r})\}$ that gives an energy less than the true ground-state energy. This proves that there exists a potential that can “separate off” the problematic choices for $(T, \rho(\mathbf{r}))$, which suffices to establish the existence of the maximum and its exactness. ■

The variational principle in Theorem 5 provides a way to compute the Kohn-Sham energy without using an orbital-dependent kinetic-energy functional, as is common in the Kohn-Sham procedure. The cost of such a method, of course, resembles the Kohn-Sham procedure instead of a typical orbital-free methodology.

The max-min principle may have importance in formal theory, however. Ref. [54] shows that the separating hyperplane, (37), is proportional to the functional derivative of the energy expression with respect to its arguments, evaluated at the minimizing (ground-state) values. This means that the hyperplane has the form

$$\left(\frac{\partial E_v[\rho_{g.s.}; T_{g.s.}]}{\partial T} \right)_{\rho_{g.s.}(\mathbf{r})} T + \int \left(\frac{\partial E_v[\rho_{g.s.}; T_{g.s.}]}{\rho(\mathbf{r})} \right)_{T_{g.s.}} \rho(\mathbf{r}) \geq \alpha. \quad (39)$$

Evaluating the functional derivative and choosing the proportionality constant to be

$$\left[\left(\frac{\partial E_v[\rho_{g.s.}; T_{g.s.}]}{\partial T} \right)_{\rho_{g.s.}(\mathbf{r})} \right]^{-1},$$

the equation for the hyperplane is

$$T + \int \rho(\mathbf{r}) v_{KS}(\mathbf{r}) d\mathbf{r} \geq E_s[v_{KS};N], \quad (40)$$

where the Kohn-Sham potential, the Coulomb potential, and the exchange-correlation potentials have been defined in the usual ways,

$$v_{KS}[\rho_{g.s.}; \mathbf{r}] = v(\mathbf{r}) + v_J[\rho_{g.s.}; \mathbf{r}] + v_{xc}[\rho_{g.s.}; \mathbf{r}], \quad (41)$$

$$v_J[\rho_{g.s.}; \mathbf{r}] = \int \frac{\rho_{g.s.}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (42)$$

$$v_{xc}[\rho_{g.s.}; \mathbf{r}] = \frac{\delta E_{xc}[\rho_{g.s.}]}{\delta \rho(\mathbf{r})}. \quad (43)$$

Inserting this result into Eq. (33),

$$E_{g.s.}[v; N] = \min_{\{\tilde{T}, \tilde{\rho} | \tilde{T} + \langle \tilde{\rho} v_{KS} \rangle \geq E_s[v_{KS}; N]\}} \left(\tilde{T} + \int \tilde{\rho}(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + J[\tilde{\rho}] + E_{xc}[\tilde{\rho}] \right). \quad (44)$$

Equation (44) has a simple and important interpretation.

Theorem 6: Upper bounds from the Kohn-Sham energy. Suppose that $T_c[\rho] + V_{ee}[\rho] = J[\rho] + E_{xc}[\rho]$ is a convex functional. If the choice of electron density and the choice of kinetic-energy functional provide an upper bound to the ground-state energy of the noninteracting system,

$$E_s[v_{KS}; N] \leq \tilde{T}[\tilde{\rho}] + \int \tilde{\rho}(\mathbf{r}) v_{KS}(\mathbf{r}) d\mathbf{r}, \quad (45)$$

then they also provide an upper bound to the ground-state energy of the interacting system,

$$E_{g.s.}[v; N] \leq \tilde{T}[\tilde{\rho}] + \int \tilde{\rho}(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + J[\tilde{\rho}] + E_{xc}[\tilde{\rho}]. \quad (46)$$

This result does not seem to be known, perhaps because it requires assuming that $J[\rho] + E_{xc}[\rho]$ is convex. It is not known whether this assumption is valid. However, in Sec. III it will be argued that if one uses meta-GGAs [57–69], then $J[\rho] + E_{xc}[\rho; t]$ should be convex with respect to both the electron density $\rho(\mathbf{r})$ and the kinetic energy density $t(\mathbf{r})$. For conventional density-only functionals, one might expect that because $J[\rho]$ is convex and the Coulomb energy is much larger than the exchange-correlation energy in many-electron systems, that $J[\rho] + E_{xc}[\rho]$ is convex. No rigorous mathematical argument for this is known, however, and many approximate functionals (e.g., the local density approximation) fail to satisfy this constraint [70].

C. Practical N -representability conditions for the kinetic energy functional

Theorem 4 is our most practical result. It indicates that kinetic-energy functionals should satisfy the constraint

$$\tilde{T}_s[\rho] + \int \rho(\mathbf{r}) v_s(\mathbf{r}) d\mathbf{r} \geq E_s[v_s; N] \quad (47)$$

for every choice of electron density and every choice of noninteracting potential. This is a very stringent constraint. Equation (47) will only be true if the “orbital-free” ground-state energy of this noninteracting system is above the true ground-state energy. This means that a necessary condition for the N -representability of the approximate kinetic energy functional $\tilde{T}_s[\rho]$ is that

$$\min_{\substack{\langle \rho \rangle = N \\ \rho(\mathbf{r}) \geq 0}} \tilde{T}_s[\rho] + \int \rho(\mathbf{r}) v_s(\mathbf{r}) d\mathbf{r} \geq E_s[v_s; N] \quad (48)$$

for every $v_s(\mathbf{r})$.

In its most general form, this constraint is not very practical because it requires determining the ground state of reference systems of noninteracting electrons. (This, of course, is exactly what we wish to avoid doing by using orbital-free DFT methods.) However, there are some systems of noninteracting electrons for which analytic results for the N -electron energy are known, including (a) electrons confined in a rectangular box; (b) electrons confined in a harmonic oscillator; (c) electrons confined in an atomic $[v_s(\mathbf{r}) = -Z/r]$ potential; (d) electrons confined in a spherical box; and (e) electrons confined in a diatomic potential (using results known for H_2^+ and its higher-atomic-number congeners).

In general, any potential for which the first $N/2$ one-electron eigenvalues can be determined exactly is a possible reference state. For example, if we wanted to construct an approximate kinetic-energy functional $\tilde{T}_s[\rho]$ for the xenon atom ($N=54$), we might seek to satisfy the following constraints.

(a)

$$\min_{L>0} \tilde{T}_s[\rho] + 54 - \frac{732\pi^2}{2L^2} \geq 0. \quad \left\{ \begin{array}{l} \rho(\mathbf{r}) \geq 0; \langle \rho \rangle = 54 \\ \rho(\mathbf{r}) = 0 \text{ if } \mathbf{r} \notin [0, L]^3 \end{array} \right\}$$

(In this optimization, the electron density is forced to be zero outside the cubical box.)

(b)

$$\min_{\omega>0} \tilde{T}_s[\rho] + \int \frac{\omega^2 r^2}{2} \rho(\mathbf{r}) d\mathbf{r} - 227\omega \geq 0. \quad \{\rho | \rho(\mathbf{r}) \geq 0; \langle \rho \rangle = 54\}$$

(c)

$$\min_{Z>0} \tilde{T}_s[\rho] - \int \frac{Z\rho(\mathbf{r})}{r} d\mathbf{r} + \frac{61}{16} Z^2 \geq 0. \quad \{\rho | \rho(\mathbf{r}) \geq 0; \langle \rho \rangle = 54\}$$

Since the inequalities in the form (48) must hold for every electron density and every possible choice of the parameters that define the potential, optimizing the inequality with respect to the parameters that define the potential is desirable. There are, of course, many possible potentials beyond those considered here. In order to enforce constraints based on those potentials, a small calculation (to determine the reference energy) would have to be done at the very beginning of the procedure.

Necessary conditions like the ones listed here might be very useful in orbital-free DFT. If one is given a kinetic energy functional that depends on some parameters, these parameters could be selected so that conditions like (a), (b), and (c) are satisfied as accurately as possible. For example, if one is planning to use Thomas-Fermi-like theory to describe a quantum dot of electrons confined to a box or a harmonic well, it will be sensible to parametrize the kinetic-energy functional so that it satisfies the constraints for noninteracting electrons confined by similar wells [71,72]. If one wishes

to design kinetic-energy functionals for atomic systems, it will be especially important to ensure that the constraints pertaining to atomic potentials are satisfied. According to Theorem 6, if you use the Kohn-Sham potential to define the constraint, then kinetic-energy functionals that satisfy the constraint will give energies above the true ground-state energy. This is not a practical way to proceed, but it demonstrates that the “criterion for goodness” in Eq. (48) is that the constraining potential(s) resembles the Kohn-Sham potential as much as possible.

It should be noted that all of the most common explicit kinetic-energy functionals are non- N -representable. For example, the Weizsacker kinetic energy is N -representable for one- and two-electron systems, but not for systems with three or more electrons. (The Weizsacker kinetic energy is a rigorous lower bound to the Kohn-Sham kinetic energy for $N \geq 3$.) The Thomas-Fermi kinetic-energy functional is not N -representable either. (Even for one-electron systems, if the electron density is highly oscillatory but the electron density is always small, then the Thomas-Fermi kinetic energy will be far below the true kinetic energy.) Commonly one attempts to correct the Thomas-Fermi kinetic energy by adding λ times the Weizsacker form to it, giving the TF+ λ W kinetic energy functional. (Typical choices are $\lambda = \frac{1}{9}$ and $\frac{1}{5}$.) For $\lambda < 1$, this kinetic-energy functional is not N -representable for the same reason that the ordinary Thomas-Fermi kinetic-energy functional is not N -representable (i.e., TF+ λ W fails for systems with highly oscillatory electron densities). The reader will not be surprised to learn, then, that if one uses these functionals to evaluate the kinetic energy for the ground-state electron density of the xenon atom, one gets results that are far below the true answer: $T_W = 2932E_h$, $T_{TF} = 6858E_h$, $T_{TF+W/9} = 7083E_h$, $T_{\text{accurate}} = 7232E_h$. The failures of the conventional functionals serve to emphasize how important it is to consider N -representability constraints when developing new types of kinetic-energy functionals.

N -representability conditions on the kinetic-energy functionals offer new prospects for orbital-free (also called “density-only”) approaches to DFT, where the kinetic energy is written as an explicit functional of the electron density. The allure of such approaches is clear: because the spatial extent of the electron density directly reflects the size of the molecule, approaches that compute the energy directly from the electron density achieve linear scaling in a straightforward and extremely computationally efficient way. Because orbital-free density-functional theory (OFDFT) approaches need not deal with orbitals (the mainstay of “divide-and-conquer” approaches [73]) or density matrices (the nearsightedness of which is exploited by direct minimization techniques [74,75]), they are much more efficient. In fact, the computational cost of OFDFT calculations scales linearly with the *volume* of the system, rather than with the number of electrons. Thus the cost of all-electron calculations for lithium metal clusters (three electrons/atom) and rubidium metal clusters (37 electrons/atom) would be similar in OFDFT. This is “too good to be true” and, using existing functionals, the latter calculation would be extremely inaccurate. In practice, OFDFT calculations subsume almost all of the electrons into a pseudopotential [76], reducing the electron density so that the approximate kinetic-energy func-

tionals act as if “more N -representable.” At this point, of course, the cost benefit of orbital-free calculations over linear-scaling Kohn-Sham approaches is diminished. It is hoped that, by using the N -representability conditions, reliable orbital-free kinetic energy functionals for many-electron systems can be developed. Since the N -representability constraints become increasing stringent as the number of electrons increases [51,77], however many-electron systems will probably be significantly more difficult to model than few-electron systems of the same size.

D. N -representability constraints for the exchange-correlation energy

The most severe N -representability problem for density-functional theory is the kinetic-energy functional. It seems very difficult to develop a kinetic-energy density functional that incorporates the increasing complexity of electronic structure with increasing N . This motivates the Kohn-Sham approach to density-functional theory [78] and also Ludeña’s work on using the local scaling transformation method to construct N -representable kinetic-energy functionals [25,79,80].

In the Kohn-Sham approach, the kinetic energy is approximated using the noninteracting reference system. One then defines the exchange-correlation energy to be the “unknown” part of the kinetic energy plus the unknown part of the Coulomb energy,

$$E_{xc}[\rho] = T_c[\rho] + V_{ee}[\rho] - J[\rho], \quad (49)$$

where the correlation kinetic energy is defined by Eq. (29) and

$$J[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (50)$$

In the Kohn-Sham approach, the only part of the energy functional that is approximated is $E_{xc}[\rho]$. One might expect that, since the exchange-correlation energy is much smaller than the kinetic energy, the N -representability of the exchange-correlation functional is not very important. While this is the conventional view (though it was never universally accepted [21–23]), recent work suggests that non- N -representable exchange-correlation functionals can have qualitatively incorrect behavior, and generally describe molecule dissociation and symmetry breaking in unsatisfactory ways. In particular, non- N -representable exchange-correlation functionals are associated with many-electron self-interaction error [24].

The necessary and sufficient conditions for $E_{xc}[\rho]$ to be N -representable follow directly from necessary and sufficient conditions on the Hohenberg-Kohn functional $F[\rho]$.

Theorem 7: Necessary and sufficient conditions for N -representable $E_{xc}[\rho]$. An approximate functional $\tilde{E}_{xc}[\rho]$ is N -representable if and only if

$$\tilde{E}_{xc}[\rho] \geq E_{g.s.}[w;N] - \int \rho(\mathbf{r})w(\mathbf{r})d\mathbf{r} - J[\rho] - T_s[\rho] \quad (51)$$

for every electron density $\rho(\mathbf{r})$ and every external potential $w(\mathbf{r})$.

Note that the density functionals on the right-hand side of Eq. (51) can be evaluated exactly for any given electron density. In particular, the Kohn-Sham kinetic energy can be evaluated using the Zhao-Morrison-Parr method [81,82] or the Legendre transform technique in Eq. (28) [19,83].

A direct corollary of Theorem 7 is that an approximate exchange-correlation $\tilde{E}_{xc}[\rho]$ is N -representable if and only if the energy computed via the Kohn-Sham method

$$\tilde{E}_v[\rho] = T_s[\rho] + J[\rho] + \tilde{E}_{xc}[\rho] + \int \rho(\mathbf{r})w(\mathbf{r})d\mathbf{r} \geq E_{g.s.}[w;N] \quad (52)$$

is always greater than the true ground-state energy for any choice of external potential. Based on this criterion, it seems that none of the commonly employed density functionals are N -representable.

III. EXTENSION TO ENERGY DENSITIES

A. Density functionals for the kinetic-energy density

Most density functionals are expressed as integrals over energy densities. This can be somewhat problematic: there are many possible definitions for the energy density, all of which will integrate to the correct total energy (or a component thereof). Nonetheless, as long as one defines exactly what one means by an energy density, then one can derive N -representability constraints for this quantity.

As an example of the general strategy that one uses to derive N -representability constraints on energy densities, we

will present results for two different choices for the kinetic energy density, the conventional choice [84–89]

$$t_s^{(a)}(\mathbf{r}_1) = N \sum_i \frac{p_i}{2} \langle \Phi_i | -\nabla_1^2 | \Phi_i \rangle_{2,3,\dots,N} \quad (53)$$

and a positive-definite kinetic-energy density [88–90]

$$t_s^{(b)}(\mathbf{r}_1) = N \sum_i \frac{p_i}{2} \langle \nabla_1 \Phi_i | -\nabla_1 \Phi_i \rangle_{2,3,\dots,N} = t_s^{(a)}(\mathbf{r}_1) - \frac{1}{4} \nabla^2 \rho(\mathbf{r}). \quad (54)$$

Here the notation $\rangle_{2,3,\dots,N}$ indicates integration with respect to the second, third, ..., N th electronic coordinates; the first electronic coordinate is not integrated over, and so

$$T_s = \int t_s^{(a)}(\mathbf{r}_1) d\mathbf{r}_1 = \int t_s^{(b)}(\mathbf{r}_1) d\mathbf{r}_1. \quad (55)$$

The reader is referred to Ref. [90] for a review of these and other forms for the local kinetic energy.

The necessary and sufficient conditions for the N -representability of the local kinetic energy depend on the particular form one chooses.

Theorem 8. A given choice for the noninteracting kinetic energy density and the electron density are mutually N -representable if and only if

$$\int \xi(\mathbf{r}) t_s^{(a)}(\mathbf{r}) d\mathbf{r} \geq E_s^{(a)}[v_s, \xi; N] - \int \rho(\mathbf{r}) v_s(\mathbf{r}) d\mathbf{r}, \quad (56)$$

$$\int \xi(\mathbf{r}) t_s^{(b)}(\mathbf{r}) d\mathbf{r} \geq E_s^{(b)}[v_s, \xi; N] - \int \rho(\mathbf{r}) v_s(\mathbf{r}) d\mathbf{r} \quad (57)$$

for every potential $v_s(\mathbf{r})$ and every “local weighting” $\xi(\mathbf{r})$ of the kinetic energy. Here, the noninteracting energy bifunctionals are defined as

$$E_s^{(a)}[v_s, \xi; N] = \min_{p_i, \Phi_i} \left[\sum_i p_i \langle \Phi_i | \sum_{j=1}^N \left\{ \xi(\mathbf{r}) \left(-\frac{\nabla_j^2}{2} \right) + v_s(\mathbf{r}_j) \right\} | \Phi_i \rangle \right], \quad (58)$$

$$E_s^{(b)}[v_s, \xi; N] = \min_{p_i, \Phi_i} \left(\sum_i p_i \left[\langle \Phi_i | \sum_{j=1}^N \left\{ \xi(\mathbf{r}) \left(-\frac{\nabla_j^2}{2} \right) + v_s(\mathbf{r}_j) \right\} | \Phi_i \rangle + \left\langle \sum_{j=1}^N \left\{ \xi(\mathbf{r}) \left(-\frac{\nabla_j^2}{4} \right) | \Phi_i \right\}^2 \right\rangle \right] \right). \quad (59)$$

The proof of this theorem is analogous to the proof of Theorem 5.

The necessary conditions on the kinetic energy that were presented in Sec. II C are also necessary conditions for the kinetic-energy density. However, those conditions are rather weak, since they depend only on the integral of the kinetic-energy density, and not the local value. [Unlike the necessary and sufficient conditions, Eqs. (58) and (59), the conditions in Sec. II C do not depend on the particular form of the

kinetic-energy density.] There is a growing literature on finding the eigenvalues and eigenvectors of Hamiltonians with the form of Eq. (58); such Hamiltonians are said to have a position-dependent effective mass [91–102]. The results of those computations could be used to develop necessary conditions for the N -representability of $t_s^{(a)}[\rho; \mathbf{r}]$ that are analogous to the constraints in Sec. II C. The authors are not aware of any results that would provide constraints on the positive-definite kinetic-energy density $t_s^{(b)}(\mathbf{r})$.

B. Constraints on meta-GGAs

It is important to be able to model the kinetic-energy density because most orbital-free kinetic-energy functionals are based on modeling the kinetic-energy density. However, models for the kinetic-energy density are also important in Kohn-Sham DFT, because the kinetic-energy density is the essential ingredient of the meta-generalized-gradient-approximation (meta-GGA) family of density functionals. Accurate orbital-free models for the kinetic-energy density would permit meta-GGAs to be rewritten as simpler (and computationally faster) GGAs. (This sort of transformation plays an essential role in the derivation of the Lee-Yang-Parr functional [60], for example.)

Our construction also has direct implications for the properties of meta-GGA functionals, and thus provides constraints that can guide the construction of new and improved meta-GGAs. If the energy is written as a bifunctional of the kinetic energy density and the electron density, then the variational principle can be restated as

$$\int t(\mathbf{r})d\mathbf{r} + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + J[\rho] + E_{xc}[\rho, t] \geq E_{g.s.}[v; N]. \quad (60)$$

For any N -representable $(t(\mathbf{r}), \rho(\mathbf{r}))$, the necessary and sufficient condition for the N -representability of a meta-GGA functional is that the equality must be satisfied for every external potential. Equivalently,

$$J[\rho] + E_{xc}[\rho, t] \geq E_{g.s.}[v; N] - \int t(\mathbf{r})d\mathbf{r} - \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r}. \quad (61)$$

Equation (61) must be true for every external potential and every N -representable $(t(\mathbf{r}), \rho(\mathbf{r}))$.

Taking the supremum of the right-hand side with respect to the free variable gives an exact construction for a meta-GGA, namely,

$$J[\rho] + E_{xc}[\rho, t] \geq \sup_{v(\mathbf{r})} \left(E_{g.s.}[v; N] - \int t(\mathbf{r})d\mathbf{r} - \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \right) \quad (62)$$

or

$$E_{xc}[\rho; t] \geq \left[\sup_{v(\mathbf{r})} \left(E_{g.s.}[v; N] - \int t(\mathbf{r})d\mathbf{r} - \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \right) \right] - J[\rho]. \quad (63)$$

The preceding formula is a sort of “restricted” Legendre transformation [36]. Equation (63) is the exact meta-GGA functional for normal electronic systems. [Equation (63) is not exact for Hamiltonians with a position-dependent effective mass, though the equation is easily adapted to such systems by incorporating the appropriate dependence on $\xi(\mathbf{r})$.]

Because (a) the argument of the supremum is a linear functional of $t(\mathbf{r})$ and $\rho(\mathbf{r})$ and (b) the supremum of a sum is less than the sum of the suprema, Eq. (62) implies that (i) $E_{xc}[\rho, t]$ is a convex functional of the kinetic-energy density

and (ii) $J[\rho] + E_{xc}[\rho; t]$ is a convex functional of the electron density. For approximate functionals that are differentiable, statements (i) and (ii) require that the second derivative with respect to the local kinetic energy and the electron density be positive. That is,

$$\frac{\delta E_{xc}[\rho, t]}{\delta t(\mathbf{r}) \delta t(\mathbf{r}')} \geq 0, \quad (64)$$

$$\frac{\delta E_{xc}[\rho, t]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \geq - \frac{1}{|\mathbf{r} - \mathbf{r}'|}. \quad (65)$$

These statements not only provide constraints for the construction of meta-GGAs, they offer a rationale for the convexity assumption in Theorem 5. Specifically, in Eq. (32), replace $E_{xc}[\rho]$ with a properly constructed meta-GGA functional $E_{xc}[\rho, t]$. Then $J[\rho] + E_{xc}[\rho, t]$ will be convex with respect to both $\rho(\mathbf{r})$ and $t(\mathbf{r})$, and the hypotheses of Theorem 5 will be automatically satisfied. By analogy, it is reasonable—but not certain—to expect that $J[\rho] + E_{xc}[\rho]$ is a convex functional even when a pure density functional, and not a meta-GGA, is used in Eq. (32).

IV. SUMMARY

This paper seeks to clarify the nature of the N -representability problem for density functionals. Necessary and sufficient conditions are presented for the N -representability of the Hohenberg-Kohn function $F[\rho] = T[\rho] + V_{ee}[\rho]$ (Theorem 1); the electron-electron repulsion energy function $V_{ee}[\rho]$ (Theorem 3); the kinetic-energy functional $T[\rho]$ (Theorem 4); the exchange-correlation energy functional $E_{xc}[\rho]$ (Theorem 7); the local kinetic-energy density $t(\mathbf{r})$ (Theorem 8); and meta-GGA-type functionals (see Sec. III B).

In addition to these results, Sec. II C provides some explicit necessary (but not sufficient) conditions for the N -representability of the kinetic-energy functional. These constraints should be useful for constructing and testing new kinetic-energy density functionals. It is also potentially useful to know that if a kinetic-energy functional that provides an upper bound to the energy of the noninteracting system with a given potential $w(\mathbf{r})$, then that kinetic-energy functional also provides an upper bound to the interacting system whose Kohn-Sham potential is equal to $w(\mathbf{r})$ (see Theorem 6).

In addition to these explicit results on N -representability, we derived an alternative to the usual Kohn-Sham method, which proceeds without using an orbital-dependent representation of the kinetic energy (Theorem 5).

The most severe N -representability problem in density-functional theory is certainly related to the kinetic energy, and for this reason the authors have focused on kinetic energy functionals and related quantities (Theorems 4–6 and 8). Because the N -representability problem for kinetic-energy functionals is so difficult, most practical density-functional theory calculations use the Kohn-Sham procedure. In the Kohn-Sham method, the kinetic energy is written as a

composite functional of the electron density. (The kinetic energy is an explicit function of the Kohn-Sham orbitals, which are functionals of the Kohn-Sham potential, which is a functional of the electron density.) This construction ensures that the Kohn-Sham kinetic-energy functional is N -representable. But this does not mean that there is no N -representability problem in Kohn-Sham density-functional theory. The problem, however, is confined to the exchange-correlation energy functional. (In particular, the non- N -representability of the exchange-correlation energy functional is associated with the problem of self-interaction error [24].) In Sec. III B, we derived some specific constraints related to the N -representability of one particular class of exchange-correlation functionals, the meta-GGAs. In particular, we showed that meta-GGAs should be chosen to be *convex* functionals of the local kinetic-energy density. In practice, this means that the second functional derivative of meta-GGAs with respect to the kinetic-energy density should be positive [cf. Eq. (64)]. This constraint seems to be satis-

fied by the simplest meta-GGAs [57,103]. However, the corresponding constraint on the second functional derivative with respect to the electron density, Eq. (65), does not seem to be satisfied.

Theorem 7 provides necessary and sufficient conditions for the N -representability of the exchange-correlation energy functional. It would be interesting to examine how well existing functionals satisfy these constraints. However, we can say, with certainty, that any exchange-correlation functional that ever gives an energy below the true ground-state energy for any electronic system is not N -representable. Based on this criterion, it seems that none of the popular exchange-correlation energy functionals are N -representable.

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