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Axiomatic formulations of the Hohenberg-Kohn functional

Paul W. Ayers
Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1

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Properties of the Hohenberg-Kohn functional are considered. In particular, the Hohenberg-Kohn functional should (a) give correct results in the variational principle and should be (b) continuous, (c) convex, and (d) size consistent. All of these properties are satisfied by the Legendre-transform functional (equivalently, the density matrix constrained search functional) and, moreover, this is the only functional that possesses all these properties. Not only that, but the Legendre-transform functional is determined uniquely by requiring (a), (b), and either (c) or (d). This shows how an "axiomatic" approach to constructing the Hohenberg-Kohn functional leads naturally to the Legendre-transform functional. Among all functionals consistent with the variational principle, the Legendre-transform functional is the smallest. One corollary to this approach is a simple proof of the equivalence of the Legendre-transform and density-matrix constrained search functionals. For completeness, the Appendix shows that ensemble-v-representable densities lie dense in the set of N-representable densities.

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I. INTRODUCTION

Density-functional theory (DFT) has established itself as the dominant approach to computational electronic structure theory for large molecules, clusters, and solids [1–4]. Indeed, at this stage much of the language of chemistry and physics is based on density-functional theory, so that even when density-functional theoretic methods are not used, computational results are often described using terminology associated with DFT.

From the very beginning, it was recognized that density-functional theory is mathematically subtle and that, moreover, understanding these mathematical subtleties is important for the development of more accurate functionals. It is a testament to these subtleties that, even now, multiple definitions of the exact functional are in use, chiefly the wave-function constrained search functional of Levy [5], the density-matrix constrained search of Valone [6], and the Legendre-transform functional of Lieb [7] (which is equivalent to the density-matrix constrained search) [7]. Any approximate density functional can be viewed as an approximation of one of the exact functionals, though often it is not at all clear which of the exact functionals is being approximated. In any event, one approach for improving the quality of approximate functionals is to require the approximate functionals to mimic the mathematical properties of the exact functionals. This approach requires that one decide which exact functional is to be approximated. In deciding which exact functional will be approximated, it is very helpful to explore the mathematical properties of the exact functionals, as these yield constraints that approximate functionals should satisfy.

Since there is no unique definition of the exact density functional, formal analysis must always start with the question: what is the best exact functional for a particular purpose? When faced with such a question, it is usually clear that it is desirable for the functional to have certain mathematical characteristics, but unclear whether a functional with the desired characteristics exists and, if such a functional does exists, whether it is unique. That is, one needs to define a functional based on a set of desired properties, a task that is arguably more difficult that determining the properties of a given functional. This is the essence of an axiomatic formulation: one defines the "axioms" that define the parameters of the theory, and then one determines what theory (if any) satisfies the axioms.

Axiomatic constructions usually start by compiling a list of desiderata—e.g., mathematical properties that we would like the exact functional to satisfy—and exploring how these axioms restrict the possible definitions. Sometimes no functional can satisfy all these properties; in this case the proposed set of axioms is said to be inconsistent. Even where the set of axioms is consistent, sometimes only a few of the desired properties are required to fully specify the functional, at which point the other desired properties are automatically fulfilled; in this case, the superfluous axioms are said to be redundant. The strength of the axiomatic approach is that the assumptions underlying the analysis are clear, and the functionals obtained are defined not by how they are constructed (there can be many ways to construct the same functional, as is clear from the fact that the density-matrix constrained search [6] and the Legendre-transform [7] approaches give identical functionals [7]) but by the mathematical properties the functionals possess. This extricates arguments over "which functional is best" from the algorithmic ambiguities of how a functional is constructed, so that the "best" functional for a specific application can be simply identified: the best functional is the one with the most useful mathematical properties. Clearly, different applications may warrant different functionals.

In this paper, an axiomatic approach to the Hohenberg-Kohn functional is proposed. Specifically, in this paper a functional is constructed that is (a) consistent with the variational principle, (b) continuous, (c) convex, and (d) functionally size-consistent.

To show this, the proposed functional is first defined for v-representable densities (Sec. II), and then—always taking care to fulfill the above properties—the domain of definition is expanded to include ensemble-v-representable densities (Sec. III) and then non-v-representable densities (Sec. IV). The resulting functional is the smallest possible functional consistent with the variational principle, which shows that it must be identical with the Legendre transform functional (Sec. V). The axiomatically-constructed functional is also identical to the density-matrix constrained search functional. Section VI elaborates on a few facts germane to the present discussion.

Some confusion might arise between the present work and the recent work of Pan, Sahni, and Massa [8,9]. The vocabulary of this paper and those papers is superficially similar because both papers are concerned with developing functionals that have certain desired "properties." In the work of Pan, Sahni, and Massa, however, the properties of interest are typically physical observables, and the constrained search is used to construct functionals that give specified values for those observables. [Their work, then, is just the direct generalization of the original constrained search (in which the property of interest was the electron density or density matrix) [5].] Their approach is not axiomatic; for example, using ensembles instead of wave functions in the constrained search would give different functionals. In contrast to their emphasis on observable properties of electronic systems, this paper is concerned with *formal mathematical properties* of the Hohenberg-Kohn functional. The approach of this paper is axiomatic: starting with a set of formal mathematical traits that we desire for the functional to possess, a functional that possesses those traits will be developed in a way that is independent of any particular method of functional construction (e.g., the constrained search formulation).

II. v-REPRESENTABLE DENSITIES

The most important and fundamental properties of density functionals date were already clear in the seminal work of Hohenberg and Kohn [10]. Certainly, for any system, we wish for the Hohenberg-Kohn functional—defined as the sum of the kinetic and electron-electron repulsion energies—to give the exact energy. The total energy of the system with external potential $v(\boldsymbol{r})$ and electron density $\rho(\boldsymbol{r})$ is defined as

$$E_v[\rho] = F[\rho] + \int \rho(\boldsymbol{r})v(\boldsymbol{r})d\boldsymbol{r}, \tag{1}$$

with

$$F[\rho] = T[\rho] + V_{ee}[\rho]. \tag{2}$$

Requiring the energy to be exact means that if $\rho_v(\boldsymbol{r})$ is the electron density resulting from a N-electron ground-state wave function for the external potential $v(\boldsymbol{r})$, then

$$F_{HK}[\rho_v] = E[v,N] - \int \rho_v(\boldsymbol{r})v(\boldsymbol{r})d\boldsymbol{r}, \tag{3}$$

where $E[v,N]$ is the system's ground state energy. Any functional satisfying Eq. (3) is said to be *exact*.

From the beginning, it was recognized that Eq. (3) might not adequately define the fundamental density functional, $F[\rho]$ [10]. The difficulty arises because the ground state energy and density are usually determined by minimizing the energy functional, Eq. (1) with respect to all N-electron densities. The ground state energy is then the smallest value of the energy,

$$E_{g.s.} = \min_{\langle\rho(\boldsymbol{r})\rangle=N} E_v[\rho] = E_v[\rho_v], \tag{4}$$

and the ground state electron density is the density that yields the minimizing energy

$$\rho_v(\boldsymbol{r}) = \arg \min_{\langle\rho(\boldsymbol{r})\rangle=N} E_v[\rho]. \tag{5}$$

In the variational procedure, one minimizes with respect to all N-electron densities that are nonnegative and integrate to N electrons [7,11,12]. These candidate electron densities in the are said to be N-representable. The difficulty is that the variational principle requires that $F[\rho]$ be defined for any reasonable electron density, and not just an electron density that is the ground state for some external potential. Such ground-state densities are said to be v-representable. Mathematical nuances related to v-representable and N-representable electron densities are discussed in more detail in the Appendix.

The original Hohenberg-Kohn functional, (3), is defined only for v-representable densities. Any functional, $F[\rho]$, which gives the correct ground state energy and densities when used in Eqs. (4) and (5) and is said to be *variational*. Every variational functional is exact, but not every exact functional is variational. An example of an exact, but nonvariational, functional can be constructed from Lieb's Legendre transform functional, $F_{Legendre}[\rho]$ [cf. Eq. (26)] and Levy's constrained search functional $F_{\Psi}[\rho]$ [cf. Eq. (39)]. Specifically, the functional $F_{\text{non-var}}[\rho]=F_{Legendre}[\rho]+(F_{Legendre}[\rho]-F_{\Psi}[\rho])$ is exact, but not variational because the value of this functional for non-v-representable densities is smaller than $F_{Legendre}[\rho]$, which is the smallest allowable functional. That is, the value of $F_{\text{non-var}}[\rho]$ is too small for non-v-representable densities, so sometimes the density that minimizes the energy is not v representable. For v-representable densities, however, $F_{\text{non-var}}[\rho]=F_{Legendre}[\rho]=F_{\Psi}[\rho]=F_{HK}[\rho]$.

Given the paramount importance of the variational principle in density-functional theory, the preceding discussion has a clear implication for axiomatic formulations of the Hohenberg-Kohn functional: when extending the domain of the Hohenberg-Kohn functional to encompass non-v-representable densities, one must not compromise the variational principle.

III. ENSEMBLE-v-REPRESENTABLE DENSITIES

For almost twenty years it was believed—or at least hoped—that all "reasonable" electron densities would be v-representable. Levy and Lieb showed, however, that this is not the case [7,13]. In particular, they considered systems with g-fold degenerate ground states, where $g \geqslant 3$. For such a system, the set of v-representable densities can be quantified as

$$\rho_v^{(n)}(\boldsymbol{r}) = \sum_{i=1}^{g}\sum_{j=1}^{g} (k_i^{(n)})^* k_j^{(n)} \langle \psi_i | \hat{\rho}(\boldsymbol{r}) | \psi_j \rangle, \tag{6}$$

where $\{\psi_i\}_{i=1}^{g}$ is an orthonormal basis for the wave functions of the degenerate ground state and the expansion coefficients, $\{k_i\}_{i=1}^{g}$ are subject to the normalization constraint

$$\sum_{i=1}^{g} |k_i|^2 = 1. \tag{7}$$

Here, the density operator is

$$\hat{\rho}(\boldsymbol{r}) \equiv \sum_{i=1}^{N} \delta(\boldsymbol{r}_i - \boldsymbol{r}). \tag{8}$$

Levy and Lieb showed that if one takes g densities of the form (6) and formed the ensemble average,

$$\rho_e(\boldsymbol{r}) = \sum_{n=1}^{g} w^{(n)} \rho_v^{(n)}(\boldsymbol{r}), \tag{9}$$

where the normalization of the density is preserved (which requires $\Sigma_{n=1}^{g} w^{(n)}=1$), $w^{(n)} \geqslant 0$, and at least three of the $w^{(n)}$ are not zero, then the resulting density, $\rho_e(\boldsymbol{r})$, will not arise from the ground state wave function of any external potential. However, since this density is clearly associated with the external potential of the degenerate state, it is not "totally" non-v-representable; instead, we call such densities ensemble-v-representable.

How should one define $F[\rho]$ for ensemble-v-representable densities? One obvious choice is to select, in analogy to Eq. (3),

$$F_{ens}[\rho_e] = E[v,N] - \int \rho_e(\boldsymbol{r}) v(\boldsymbol{r}) d\boldsymbol{r}. \tag{10}$$

Choosing this definition and using Eqs. (3) and (9) and, one finds that

$$\begin{aligned} F_{ens}[\rho_e] &= \sum_{n=1}^{g} w^{(n)} \left(E[v,N] - \int \rho_v^{(n)}(\boldsymbol{r}) v(\boldsymbol{r}) d\boldsymbol{r} \right) \\ &= \sum_{n=1}^{g} w^{(n)} F_{HK}[\rho_v^{(n)}(\boldsymbol{r})]. \end{aligned} \tag{11}$$

Note that for densities that are not only ensemble-v-representable but also v-representable (the special case where one of the $w^{(n)}$ is one and all the others are zero), then $F_{ens}[\rho_e]$ is equivalent to the original Hohenberg-Kohn functional, Eq. (3).

Yang, Zhang, and Ayers showed that Eq. (11) is a consequence of *functional size consistency* [14]. A functional, $Q[\rho]$, is said to be functionally size consistent if, given a set of p densities that are infinitely far apart,

$$Q\left[\sum_{n=1}^{p} \rho_v^{(n)}\right] = \sum_{n=1}^{p} Q[\rho_v^{(n)}]. \tag{12}$$

Equation (12) is consistent with the fact that electronic systems that are infinitely far apart do not interact. If $F[\rho]$ is functionally size consistent, then Eq. (11) must hold.

It is important to note that $F_{ens}[\rho]$ gives the smallest possible values for ensemble-v-representable densities. That is:

Theorem 1. If $F[\rho]$ is variational, then $F[\rho_e] \geqslant F_{ens}[\rho_e]$ for all ensemble-v-representable densities, $\rho_e(\boldsymbol{r})$.

Proof. Suppose that $F[\rho_e] < F_{ens}[\rho_e]$. Using the fact that $\Sigma_{n=1}^{p} w^{(n)}=1$ and the definition of $F_{ens}[\rho]$ [Eq. (11)], we have that

$$\begin{aligned} E[v,N] &= \sum_{n=1}^{p} w^{(n)} E[v;N] \\ &= \sum_{n=1}^{p} w^{(n)} \left(F_{HK}[\rho_v^{(n)}] + \int \rho_v^{(n)}(\boldsymbol{r}) v(\boldsymbol{r}) d\boldsymbol{r} \right) \\ &= F_{ens}[\rho_e] + \int \rho_e(\boldsymbol{r}) v(\boldsymbol{r}) d\boldsymbol{r} \\ &> F[\rho] + \int \rho_e(\boldsymbol{r}) v(\boldsymbol{r}) d\boldsymbol{r}. \end{aligned} \tag{13}$$

Consequently,

$$E[v;N] > \min_{\langle\rho\rangle=N} F[\rho] + \int \rho(\boldsymbol{r}) v(\boldsymbol{r}) d\boldsymbol{r} \tag{14}$$

and so $F[\rho]$ is not variational, contrary to our original assumption. ■

It is possible for $F[\rho]$ to be exact and variational but have $F[\rho_e] > F_{ens}[\rho_e]$ for some ensemble-v-representable electron densities. In fact, Levy's wave-function constrained search functional satisfies this inequality [5,15]. This property of Levy's wave-function constrained search is explored in more detail at the end of this paper; see Eq. (39) and the subsequent discussion.

A functional is said to be convex if

$$Q\left[\sum_{n=1}^{p} w^{(n)} \rho^{(n)}(\boldsymbol{r})\right] \leqslant \sum_{n=1}^{p} w^{(n)} Q[\rho^{(n)}(\boldsymbol{r})] \tag{15}$$

whenever $0 \leqslant w^{(n)}$ and $\Sigma_{n=1}^{p} w^{(n)}=1$. Clearly, if $F[\rho_e] > F_{ens}[\rho_e]$, then $F[\rho_e]$ is not convex. Consequently, Levy's constrained search functional is not convex. Since the inequality in Eq. (15) is forbidden by theorem 1, we have the following.

Theorem 2. If $F[\rho]$ is both exact and functionally size consistent, then $F[\rho]=F_{ens}[\rho]$ for ensemble-v-representable densities.

Theorem 3. If $F[\rho]$ is both variational and convex, then $F[\rho]=F_{ens}[\rho]$ for ensemble-v-representable densities.

Convexity is a useful property to require because if $F[\rho]$ is convex, then the total energy functional, Eq. (1), will also be convex (since the energy is the sum of a convex functional and a linear functional). As such, the energy functional will have only one stationary point and that stationary point will be the minimum in the variational principle, which is associated with the ground state energy of the system. For systems with degenerate ground states, there will be many different minimizing densities, but even then there will be only one minimizing value of the energy. Non-convex functionals can have multiple stationary points, which can be useful in some contexts and inconvenient in others. Nonconvexity can be useful, for example, in excited-state density-functional theory: when Levy's constrained-search functional the energy can be stationary for certain special excited states [16,17]. Nonconvexity can be computational inconvenient when one is interested in the ground state, however, because variational calculations can become "trapped" in an excited state.

In this section, we have taken the original Hohenberg-Kohn functional and, by requiring either convexity or functional size consistency, constructed a unique extension of its domain of definition to encompass densities that are ensemble-v-representable.

IV. NON-v-REPRESENTABLE DENSITIES

For a short while, it was supposed that perhaps every reasonable density was at least ensemble-v-representable. Before long, however, Englisch and Englisch showed that this was not the case: there are N-representable densities that are not ensemble-v-representable [18]. We call such densities totally non-v-representable. Not only are there an infinite number of totally non-v-representable densities, but it seems that the number of totally non-v-representable densities is a dense subset of the set of all reasonable densities [18–20]. That is, for every ensemble-v-representable density, there exists a totally non-v-representable density that resembles it arbitrarily closely. Henceforth, we will often refer to "totally non-v-representable densities" as simply non-v-representable, reserving the full term for when confusion with ensemble-v-representable densities is likely to arise.

In conceptualizing the concept of a dense set, it is helpful to recall that the irrational numbers are a dense subset of the real numbers. The rational numbers are also a dense subset of the real numbers. However, the number of rational numbers is infinitely smaller than the number of irrational numbers because almost every real number is irrational. Just because the set of non-v-representable densities is dense does not imply anything about the "relative abundance" of non-v-representable densities. It is possible that almost every reasonable electron density is ensemble-v-representable; it is also possible that almost every reasonable electron density is totally non-v-representable; it is also possible that the numbers of ensemble-v-representable and totally non-v-representable densities are roughly comparable.

Insofar as there is no practical way to tell whether a density is ensemble-v-representable or not, the domain of $F[\rho]$ must be extended to encompass totally non-v-representable densities. Fortunately, Englisch and Englisch showed that the set of ensemble-v-representable densities is also a dense subset of the set of N-representable densities [19,20]. This result does not seem to be widely known, but it is of prime importance to the present paper. Because of this result's importance, the Appendix presents a different, and arguably more intuitive—albeit less mathematically rigorous—derivation.

It seems advisable to pause and reiterate the different types of electron densities that are being considered in this paper. The fundamental variational principle in density-functional theory searches over "reasonable" electron densities. Reasonable electron densities must be nonnegative and normalized to the number of electrons and, as discussed in the Appendix, it is often useful to impose further constraints on the form of reasonable electron densities. "Reasonable" electron densities are said to be N-representable because they can be associated to an N-electron wave function. Among the N-representable densities, those that are the ground state electron density for some choice of external potential have special importance; such densities are said to be v-representable, and it is these densities that feature in the original work of Hohenberg and Kohn. The set of v-representable densities can be augmented by adding to it all the electron densities that can be constructed by taking a convex linear combination of the degenerate ground-state electron densities from some external potential, Eq. (9); this gives the set of ensemble-v-representable electron densities. The set of ensemble-v-representable densities contains the set of v-representable densities and is a dense subset of the set of N-representable densities. Thus, every reasonable electron density is either ensemble-v-representable or can be approximated arbitrarily closely by an ensemble-v-representable density; this is important because every ensemble-v-representable density can be associated with a specific external potential. There are N-representable densities that are not ensemble-v-representable; these electron densities are totally non-v-representable. The set of totally non-v-representable densities is also a dense subset of the set of N-representable densities, and so every ensemble-v-representable density can be approximated arbitrarily closely by a totally non-v-representable density, and vice versa.

Mathematically, the fact that every totally non-v-representable density can be approximated arbitrarily closely by an ensemble-v-representable density implies that for any totally non-v-representable density, $\rho_t(\boldsymbol{r})$, we can find a sequence of ensemble-v-representable densities, $\rho_e^{(k)}(\boldsymbol{r})$, such that

$$\lim_{k\to\infty} \rho_e^{(k)}(\boldsymbol{r}) = \rho_t(\boldsymbol{r}). \tag{16}$$

[Equation (16) indicates that, as $k\to\infty$, the norm of $(\rho_t(\boldsymbol{r})-\rho_e^{(k)}(\boldsymbol{r}))$ approaches zero.] Based on Eq. (16), it seems logical to define $F[\rho]$ for totally non-v-representable densities as

$$F_{axiomatic}[\rho_t] \equiv \lim_{k\to\infty} F_{ens}[\rho_e^{(k)}]. \tag{17}$$

This functional is well-defined if and only if the limit exists, which requires that $F_{ens}[\rho_e^{(k)}]$ be a continuous functional on the set of ensemble-v-representable densities.

$F_{ens}[\rho]$ is a continuous functional on the set of ensemble-v-representable densities because the functional (defined on this limited set) is actually differentiable [19,20]. That is, if $\rho_e^{(\infty)}(\boldsymbol{r})$ is an ensemble-v-representable density associated with the ground state of the external potential $v^{(\infty)}(\boldsymbol{r})$, and

$\rho_e^{(k)}(\boldsymbol{r})$ is a nearby ensemble-v-representable density associated with the external potential $v_e^{(k)}(\boldsymbol{r})$, then [21]

$$F_{ens}[\rho_e^{(k)}] - F_{ens}[\rho_e^{(\infty)}] = -\int v^{(\infty)}(\boldsymbol{r})[\rho_e^{(k)}(\boldsymbol{r}) - \rho_e^{(\infty)}(\boldsymbol{r})]d\boldsymbol{r} + O(\|\rho_e^{(k)}(\boldsymbol{r}) - \rho_e^{(\infty)}(\boldsymbol{r})\|^2). \quad (18)$$

Assuming that the last term is small enough to be negligible, one has that [22]

$$|F_{ens}[\rho_e^{(k)}] - F_{ens}[\rho_e^{(\infty)}]| \le \|v^{(\infty)}(\boldsymbol{r})\| \|\rho_e^{(k)}(\boldsymbol{r}) - \rho_e^{(\infty)}(\boldsymbol{r})\|. \quad (19)$$

Thus, for any $\varepsilon > 0$, there exists a

$$\delta \lessapprox \frac{\varepsilon}{\|v^{(\infty)}\|} \quad (20)$$

such that whenever $\|\rho_e^{(k)}(\boldsymbol{r}) - \rho_e^{(\infty)}(\boldsymbol{r})\| < \delta$, then $|F_{ens}[\rho_e^{(k)}] - F_{ens}[\rho_e^{(\infty)}]| < \varepsilon$. In plain language: whenever two ensemble-v-representable densities are close together, their respective values of $F_{ens}[\rho]$ are also close together. A proof of the continuity of $F_{ens}[\rho]$ that does not use the differentiability of $F_{ens}[\rho]$ will be presented later, following the proof of theorem 8.

$F_{axiomatic}[\rho]$ is our desired functional. It is variationally stable, convex, and size-consistent. Because Eq. (17) holds whenever Eq. (16) holds, $F_{axiomatic}[\rho]$ is continuous. Unlike existing approaches, however, this construction is entirely axiomatic: $F_{axiomatic}[\rho]$ is derived from the properties we assert it to have, so that we can say the following.

Theorem 4. There is only one functional, $F_{axiomatic}[\rho]$, *that is* (a) *consistent with the variational principle*, (b) *continuous*, (c) *convex, and* (d) *size-consistent. Every functional that possesses all these properties is totally equivalent to* $F_{axiomatic}[\rho]$.

Furthermore, if we accept (a) and (b) as axioms defining the functional, then Theorems 2 and 3 indicate that axioms (c) and (d) are redundant. Thus:

Theorem 5. Axioms (a), (b) *and either* (c) *or* (d) *suffice to completely specify the functional*, $F_{axiomatic}[\rho]$.

Recapping the arguments of the preceding sections, we started by requiring that the functional gives correct answers for v-representable densities (Sec. II). Then, using convexity or size consistency, we extended the domain of definition to include ensemble-v-representable densities (Sec. III), obtaining the functional denoted $F_{ens}[\rho]$. Because the set of ensemble-v-representable densities is a dense subset of the set of all reasonable (i.e., N-representable) densities, the domain of the functional could be extended yet again by simply requiring that the functional be continuous (i.e., that nearby densities have similar values for $F[\rho]$). This procedure "fills in the holes" in the domain of $F_{ens}[\rho]$, yielding the universal functional $F_{axiomatic}[\rho]$. (This last step is analogous to how one would "naturally extend" a function defined only on the rational numbers so that its domain encompassed all real numbers.)

Here we have focused on the Hohenberg-Kohn functional, $F[\rho]$. In practical density-functional theory calculations, the Kohn-Sham formalism is usually used instead [23]. The Kohn-Sham kinetic energy functional, $T_s[\rho]$, can be defined axiomatically also. The analysis is exactly same as the preceding, but since the electrons in the Kohn-Sham reference state do not interact, the Hamiltonian for the Kohn-Sham system contains no explicit electron-electron repulsion terms and so all of the $V_{ee}[\rho]$ terms in the preceding analysis are zero. Using the axiomatic descriptions of $F[\rho]$ and $T_s[\rho]$, one can obtain an axiomatic description of the exchange-correlation functional,

$$E_{xc,axiomatic}[\rho] \equiv F_{axiomatic}[\rho] - T_{s,axiomatic}[\rho] - \frac{1}{2}\int\int \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}\, d\boldsymbol{r}'. \quad (21)$$

It should be pointed out that just because $F_{axiomatic}[\rho]$ and $T_{s,axiomatic}[\rho]$ possess a property (e.g., convexity) does not mean that $E_{xc,axiomatic}[\rho]$ will also possess that property. On the other hand, $E_{xc,axiomatic}[\rho]$ is continuous and functionally size-consistent because it is a linear combination of continuous, size-consistent, functionals. Insofar as all of the usual formulations of approximate exchange-correlation functionals give continuous, size-consistent functionals, the approximate functionals can be regarded as approximations to $E_{xc,axiomatic}[\rho]$.

One could also perform the preceding analysis at any point along the adiabatic connection path [24–27]; in that case the electron-electron repulsion terms in the Hamiltonian are neither totally neglected (as they are in the formulation of $T_{s,axiomatic}[\rho]$) or totally included (as they are in the formulation of $F_{axiomatic}[\rho]$).

V. PROPERTIES AND RELATIONSHIPS TO OTHER FUNCTIONALS

In the formal mathematical treatment of functionals, one often obtains upper bounds that depend on the norm of the functional. [For example, one often encounters inequalities like Eq. (19).] For this reason, it is convenient to define a functional that is smallest possible functional consistent with the variational principle. Fortunately, the preceding construction gives exactly this functional.

Theorem 6. Among all functionals that are consistent with the variational principle, the function defined in Sec. IV, $F_{axiomatic}[\rho]$, *is the smallest.*

Proof. Because $F_{axiomatic}[\rho] = F_{ens}[\rho]$ for all ensemble-v-representable densities, Theorem 1 asserts that $F_{axiomatic}[\rho]$ has the smallest possible value among all variational functionals for ensemble-v-representable densities.

What happens for non-v-representable densities? Suppose it were possible to define a variationally consistent functional, $F_{proposed}[\rho]$, that is smaller than the axiomatically constructed $F_{axiomatic}[\rho]$ for some non-v-representable density, $\rho_t(\boldsymbol{r})$. Let $\{\rho_e^{(k)}(\boldsymbol{r})\}$ be a sequences of ensemble-v-representable densities that converges to $\rho_t(\boldsymbol{r})$. Let $\{v^{(k)}(\boldsymbol{r})\}$ denote the sequence of external potentials associated with $\{\rho_e^{(k)}(\boldsymbol{r})\}$. Then, since $F_{axiomatic}[\rho] = F_{ens}[\rho] = E[v;N] - \int \rho(\boldsymbol{r})v(\boldsymbol{r})d\boldsymbol{r}$ for ensemble-v-representable densities,

$$F_{proposed}[\rho_t] < \lim_{k\to\infty} E[v^{(k)};N] - \int \rho_e^{(k)}(\boldsymbol{r})v^{(k)}(\boldsymbol{r})d\boldsymbol{r}. \quad (22)$$

There exists some point in the sequence at which the inequality in Eq. (22) begins to hold. That is, there exists some finite K so that for all $k > K$,

$$F_{proposed}[\rho_t] < E[v^{(k)};N] - \int \rho_e^{(k)}(\boldsymbol{r})v^{(k)}(\boldsymbol{r})d\boldsymbol{r}. \quad (23)$$

Thus, for $k > K$,

$$\begin{aligned} F_{proposed}[\rho_t] &+ \int \rho_t(\boldsymbol{r})v^{(k)}(\boldsymbol{r})d\boldsymbol{r} \\ &< E[v^{(k)};N] \\ &+ \int [\rho_t(\boldsymbol{r}) - \rho_e^{(k)}(\boldsymbol{r})]v^{(k)}(\boldsymbol{r})d\boldsymbol{r}. \end{aligned} \quad (24)$$

As $k\to\infty$, the sequence of ensemble-v-representable densities, $\{\rho_e^{(k)}(\boldsymbol{r})\}$ approaches $\rho_t(\boldsymbol{r})$, so the integral on the second line converges to zero. Thus, at some point in the sequence, the predicted energy of the non-v-representable density is less than the true ground state energy energy

$$F_{proposed}[\rho_t] + \int \rho_t(\boldsymbol{r})v^{(k)}(\boldsymbol{r})d\boldsymbol{r} < E[v^{(k)};N]. \quad (25)$$

This shows that if $F_{proposed}[\rho_t] < F_{axiomatic}[\rho_t]$, then $F_{proposed}[\rho]$ is not consistent with the variational principle. Consequently, any $F[\rho]$ that is consistent with the variational principle must be greater than or equal to $F_{axiomatic}[\rho]$. ■

Theorem 6 indicates that any functional that is smaller than $F_{axiomatic}[\rho]$ will violate the variational principle.

Theorem 6 provides the easiest way to prove that this "axiomatic" construction of $F[\rho]$ gives the same functional as the Lieb's Legendre transform functional, which is defined as the supremum over all external potentials of Hohenberg-Kohn definition [7]

$$F_{Legendre}[\rho] = \sup_{v(\boldsymbol{r})}\left(E[v;N] - \int \rho(\boldsymbol{r})v(\boldsymbol{r})d\boldsymbol{r}\right). \quad (26)$$

The key insight is that $F_{Legendre}[\rho]$ is also the smallest possible functional because if $F_{proposed}[\rho] < F_{Legendre}[\rho]$, then there exists an external potential, $w(\boldsymbol{r})$, with

$$F_{proposed}[\rho] < E[w;N] - \int \rho(\boldsymbol{r})w(\boldsymbol{r})d\boldsymbol{r} \quad (27)$$

and so

$$F_{proposed}[\rho] + \int \rho(\boldsymbol{r})w(\boldsymbol{r})d\boldsymbol{r} < E[w;N], \quad (28)$$

in contradiction to the variational principle [28,29]. Thus, every functional that is consistent with the variational principle is greater than or equal to $F_{Legendre}[\rho]$ [28,29]. From theorem 6, every functional consistent with the variational principle is greater than or equal to $F_{axiomatic}[\rho]$. It must be true, then, that:

Theorem 7. The axiomatic formulation that defines $F_{axiomatic}[\rho]$ *gives identical results to the Legendre-transform functional [Eq. (26)],*

$$F_{Legendre}[\rho] = F_{axiomatic}[\rho]. \quad (29)$$

It is often considered somewhat mysterious that the density-matrix constrained search functional introduced by Valone,

$$F_{\Gamma}[\rho] = \min_{\Gamma_N\to\rho(\boldsymbol{r})} \mathrm{Tr}[(\hat{T} + \hat{V}_{ee})\Gamma_N] \quad (30)$$

is also identical to $F_{Legendre}[\rho]$, and thus also $F_{gen}[\rho]$. In Eq. (30), the sum of the kinetic and electron-electron repulsion energies is minimized subject to the constraint that the N-electron density matrix,

$$\Gamma_N = \sum_i w_i \Psi_i(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)\Psi_i^*(\boldsymbol{r}_1', \ldots, \boldsymbol{r}_N') \quad (31)$$

$(0 \leqslant w_i \leqslant 1;\ \Sigma_i w_i = 1)$ is associated with the targeted electron density. That is, the constraint in Eq. (30) is that

$$\rho(\boldsymbol{r}) = \mathrm{Tr}[\hat{\rho}(\boldsymbol{r})\Gamma_N], \quad (32)$$

where the density operator was defined in Eq. (8). Here and in Eq. (30), the "trace" notation, $\mathrm{Tr}[\hat{Q}\Gamma_N]$, means "operate with $\hat{Q}$ on Γ_N, set the primed and unprimed variables equal, and then integrate with respect to the remaining coordinates."

Though it is well-known that $F_{\Gamma}[\rho] = F_{Legendre}[\rho]$, the usual derivation of the result requires rather sophisticated functional-analytic arguments [7]. From the present perspective, a more elementary proof can be provided.

Theorem 8. The density-matrix constrained search functional, $F_{\Gamma}[\rho]$, *and the axiomatically defined* $F_{axiomatic}[\rho]$ *are identical to each other. In light of Theorem 7, then* $F_{\Gamma}[\rho]$ *and* $F_{Legendre}[\rho]$ *are also identical.*

Proof. The starting point of this derivation is the fact that the ensemble-v-representable densities are dense. Thus, for any totally non-v-representable density, $\rho_t(\boldsymbol{r})$, there exists a sequence of ensemble-v-representable densities, $\{\rho_e^{(k)}(\boldsymbol{r})\}$, with associated potentials $\{v^{(k)}(\boldsymbol{r})\}$, such that $\rho_e^{(k)}(\boldsymbol{r}) \to \rho_t(\boldsymbol{r})$. Let $\{\Gamma_N[\rho_e^{(k)}]\}$ denote the sequence of N-electron density matrices that corresponds to the ensemble-v-representable densities $\{\rho_e^{(k)}(\boldsymbol{r})\}$. Then, using the definition of $F_{\Gamma}[\rho]$ [cf. Eq. (30)]

$$\begin{aligned} F_{\Gamma}[\rho_t] - F_{\Gamma}[\rho_e^{(k)}] &= \min_{\Gamma_N\to\rho_t(\boldsymbol{r})} \mathrm{Tr}[(\hat{T} + \hat{V}_{ee})\Gamma_N] \\ &\quad - \min_{\Gamma_N\to\rho_e^{(k)}(\boldsymbol{r})} \mathrm{Tr}[(\hat{T} + \hat{V}_{ee})\Gamma_N] \\ &= \min_{\Gamma_N\to\rho_t(\boldsymbol{r})} \mathrm{Tr}[(\hat{T} + \hat{V}_{ee})(\Gamma_N - \Gamma_N(\rho_e^{(k)}))] \\ &= \min_{\Gamma_N\to\rho_t(\boldsymbol{r})} \mathrm{Tr}\left[\left(\hat{T} + \hat{V}_{ee} + \sum_{i=1}^{N} v^{(k)}(\boldsymbol{r}_i)\right)\right. \\ &\quad \left. \times(\Gamma_N - \Gamma_N(\rho_e^{(k)}))\right] \end{aligned}$$

$$-\int (\rho_t(\boldsymbol{r})-\rho_e^{(k)}(\boldsymbol{r}))v^{(k)}(\boldsymbol{r})d\boldsymbol{r}. \tag{33}$$

Note that $\hat{T}+\hat{V}_{ee}+\Sigma_{i=1}^{N}v^{(k)}(\boldsymbol{r}_i)$ is exactly the Hamiltonian for which $\Gamma_N[\rho_e^{(k)}]$ is a ground-state N-electron density matrix, $\hat{H}[v^{(k)};N]$. So

$$F_\Gamma[\rho_t]-F_\Gamma[\rho_e^{(k)}]=\min_{\Gamma_N\to\rho_t(\boldsymbol{r})}\mathrm{Tr}[\hat{H}(v^{(k)};N)(\Gamma_N-\Gamma_N(\rho_e^{(k)}))] -\int[\rho_t(\boldsymbol{r})-\rho_e^{(k)}(\boldsymbol{r})]v^{(k)}(\boldsymbol{r})d\boldsymbol{r}. \tag{34}$$

Owing to the variational principle for the N-electron density matrix, the energy will be stationary with respect to small changes in the density matrix about $\Gamma_N[\rho_e^{(k)}]$ [30]. As the ensemble-v-representable densities, $\rho_e^{(k)}(\boldsymbol{r})$, approach $\rho_t(\boldsymbol{r})$, it will be possible to find Γ_N that give $\rho_t(\boldsymbol{r})$ that are very close to $\Gamma_N[\rho_e^{(k)}]$. The stationary principle for the energy indicates that, to first order, small changes in the density matrix about its minimal value do not change the expectation value of the energy. This then implies that the first term in Eq. (34) should become negligible as $k\to\infty$, and so

$$F_\Gamma[\rho_t]-F_\Gamma[\rho_e^{(k)}]\approx-\int[\rho_t(\boldsymbol{r})-\rho_e^{(k)}(\boldsymbol{r})]v^{(k)}(\boldsymbol{r})d\boldsymbol{r}. \tag{35}$$

As $\rho_e^{(k)}(\boldsymbol{r})\to\rho_t(\boldsymbol{r})$, the right-hand-side of Eq. (35) will approach zero, and so $F_\Gamma[\rho_e^{(k)}]\to F_\Gamma[\rho_t]$. Since the density-matrix constrained search functional, $F_\Gamma[\rho_e^{(k)}]$, has the same value as $F_{ens}[\rho_e^{(k)}]$ for ensemble-v-representable densities, this is equivalent to stating that $F_{ens}[\rho_e^{(k)}]\to F_\Gamma[\rho_t]$. Referring to Eq. (17), we recognize this as precisely the same procedure we used in the axiomatic formulation of $F_{axiomatic}[\rho]$. Thus the density-matrix based constrained search proposed by Valone and the axiomatic formulation proposed here give the same functional. ■

In the discussion of the continuity of $F_{ens}[\rho_e]$ that follows Eq. (19) it was mentioned that one can establish the continuity of $F_{ens}[\rho_e]$ without using the differentiability of this Hohenberg-Kohn functional at ensemble-v-representable densities. To do this, one traces through this argument again, but assumes this time that $\rho_t(\boldsymbol{r})$ is ensemble-v-representable, one establishes the continuity of $F_{ens}[\rho_e]$ without exploiting the differentiability of this functional. This result was alluded to in the discussion following Eq. (19). Footnote 30 discusses the exceptional case where unconventional density variations might be encountered [16], in which case; in this case the relationship in Eq. (19) is replaced by a more general proportionality,

$$|F_{ens}[\rho_e^{(k)}]-F_{ens}[\rho_e^{(\infty)}]|\propto\|\rho_e^{(k)}(\boldsymbol{r})-\rho_e^{(\infty)}(\boldsymbol{r})\| \tag{36}$$

but the same essential conclusion—$F_{ens}[\rho_e]$ is continuous on the set of ensemble-v-representable densities—still holds.

The argument in theorem 8 can also be applied to provide an alternative proof of the equivalence of the axiomatic and Legendre-transform approaches (theorem 7). Specifically, the Legendre transform functional for non-v-representable densities can be constructed as a limit of its values for ensemble v-representable densities. Specifically,

$$\begin{aligned}F_{Legendre}[\rho_t]&=\lim_{k\to\infty}\left[E(v^{(k)},N)-\int\rho_t(\boldsymbol{r})v^{(k)}(\boldsymbol{r})d\boldsymbol{r}\right]\\&=\lim_{k\to\infty}\left(F_{ens}(\rho_e^{(k)})-\left\{\int[\rho_t(\boldsymbol{r})-\rho_e^{(k)}(\boldsymbol{r})]v^{(k)}(\boldsymbol{r})d\boldsymbol{r}\right\}\right),\end{aligned} \tag{37}$$

where the term in curly brackets approaches zero as $\rho_e^{(k)}(\boldsymbol{r})$ converges to $\rho_t(\boldsymbol{r})$.

Based on Eq. (37), one might be tempted to conclude that $\rho_t(\boldsymbol{r})$ is a ground state density associated with

$$v^{(\infty)}(\boldsymbol{r})=\lim_{k\to\infty}v^{(k)}(\boldsymbol{r}). \tag{38}$$

This is true whenever the sequence of external potential converges in the appropriate norm [22], which occurs whenever $\rho_t(\boldsymbol{r})$ is ensemble-v-representable. More generally, however, $v^{(\infty)}(\boldsymbol{r})$ is not a legitimate external potential, but instead a generalized function [31]. Thus non-v-representable densities can be regarded as ground state densities for an "external potential" that is a generalized function [31]. Unfortunately, the Hohenberg-Kohn theorem does not hold for generalized functions: multiple generalized functions can have the same ground state density [31]. Nonetheless, this provides a useful way of categorizing electron densities: one starts with v-representable densities, which correspond to a ground state wave function for some external potential. This set is then expanded to encompass ensemble-v-representable densities, which correspond to a ground-state density-matrix ensemble for some external potential. The leftover electron densities are totally non-v-representable, and are ground state densities for one or more "generalized function" external potentials.

VI. DISCUSSION

By using an axiomatic approach, one can construct functionals that satisfy certain desired properties. Here, this technique is used to address the Hohenberg-Kohn density functional, $F[\rho]$, defined as the sum of the kinetic and electron-electron repulsion energies. In particular, there is only one functional that (a) satisfies the key variational principle for the electronic energy as a functional of the density, and is also (b) continuous, (c) convex, and (d) "functional" size-consistent (theorem 4). This functional, which we term $F_{axiomatic}[\rho]$, is identical to the functionals obtained using the Legendre-transform and density-matrix constrained search techniques (theorems 7 and 8). Moreover, no functional consistent with the variational principle can be smaller than this functional (theorem 6).

It is interesting to study to what extent even these constraints can be relaxed. Forcing (c) convexity and (d) size-consistency is certainly redundant (theorems 2, 3 and 5). Because the set of ensemble-v-representable densities is dense, intuition would suggest that the requirement of continuity can be relaxed, since the requirement of variational stability keeps $F[\rho]$ from getting too small for non-v-representable densities and—provided that all the non-v-representable can be written as a convex linear combination of nearby ensemble-v-representable densities—the requirement of convexity would keep $F[\rho]$ from getting too large. The author has not been able to prove this last statement, but if it is true, then axioms (a) and (c) would be sufficient by themselves. Whether the axiom of size-consistency could replace the axiom of convexity in this context is unclear.

It is clear from theorem 2 that if one forces functional size consistency, then the requirement that $F[\rho]$ be consistent with the variational principle [axiom (a)] can be replaced by the weaker requirement that $F[\rho]$ give exact results, as defined by Eq. (3), for pure-state v-representable densities. So requiring that $F[\rho]$ be exact, continuous, and size consistent is also sufficient to fully define the functional. The size consistency requirement cannot be replaced by convexity in this context, since without forcing the variational principle to hold, convexity alone does not provide enough information to specify the value of the functional for ensemble-v-representable densities.

The power of the axiomatic approach taken here is that it disentangles the particular mathematical technique or algorithm used to construct a functional from the actual definition of the functional. The author believes that the axioms chosen here are eminently reasonable. The requirement that the variational principle be satisfied and that the functional be continuous would seem beyond question: it is difficult to conceive of any useful functional that would not satisfy those key properties. The requirement of functional size consistency is also very elegant, and seems desirable. One can argue about the desirability of convexity: the results concerning unique stationary points that follow from convexity are unquestionably convenient, but also inessential. However, the convexity constraint is rendered redundant if one imposes size consistency, so these arguments are immaterial.

Traditional definitions of $F[\rho]$ seem to always satisfy the variational principle and be continuous, but are not always functional size consistent or convex. For example, the wave function constrained search proposed by Levy [5],

$$F_{\Psi}[\rho] = \min_{\Psi \to \rho(\boldsymbol{r})} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \tag{39}$$

is neither functional size consistent nor convex, yet it has played, and continues to play, an essential role in the theoretical development of density-functional theory. More generally, every functional of the form

$$F_{P[\rho]}[\rho] = P[\rho] F_{\Psi}[\rho] + (1 - P[\rho]) F_{Legendre}[\rho] \tag{40}$$

satisfies the variational principle for *any* nonnegative functional $P[\rho]$, but unless $P[\rho]=0$, $F_{P[\rho]}[\rho]$ is neither size-consistent nor convex [32]. The converse is also true; every functional that is consistent with the variational principle can be written in the form of Eq. (40) for some $P[\rho] \geqslant 0$. (If $P[\rho] \leqslant 0$ for a density that is ensemble-v-representable, then $F_{P[\rho]}[\rho]$ is not variational though, of course, it is still exact.) The fact that Eq. (40) provides a complete description of the set of variationally-consistent functionals emphasizes the vast universe of possible forms for the functional $F[\rho]$. In this context, it is rather impressive that $F_{axiomatic}[\rho]$ is completely determined by either of two choices of three simple axioms (theorem 5).

One advantage of nonconvex functionals like Eq. (40) is that higher-valued stationary points in the energy correspond to stable excited states [16,17].

Unsurprisingly, the greatest insights gleaned from the present construction are related to the Legendre-transform and density-matrix constrained search functionals. Both functionals satisfy all of the key properties here—consistency with the variational principle, continuity, functional size consistency, and convexity—and are thus not only identical to each other, but identical to any other functional that possesses these useful properties. That is, the Legendre transform and density-matrix constrained search are mathematical constructions of the same functional, and that functional is the *only* functional that satisfies the reasonable criteria studied here. At least based on these criteria, this functional should be preferred to all other functionals. It is also significant, at least conceptually, that this functional can be systematically determined from the desired properties alone, independent of any hypothetical computational ansatz. This has the obvious benefit of clarifying what assumptions are essential to the Legendre-transform–density-matrix constrained search functional (variational stability; continuity), what assumptions are optional (either convexity or size consistency), and what assumptions are totally superfluous (seemingly, everything else).

Finally, it is useful to reiterate that all of these results can be extended to the Kohn-Sham kinetic energy or, indeed, any point along the adiabatic connection path, by omitting (for the Kohn-Sham kinetic energy) or adjusting the strength of (for the adiabatic connection) the electron-electron repulsion terms. (See the discussion at the end of Sec. IV.) This allows one to construct "axiomatic" approaches to the exchange-correlation energy. It will be interesting to see what insights into the construction of approximate exchange-correlation functionals might be gleaned from the present construction. Little seems obvious, but this is definitely an area meriting future work.

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APPENDIX

The purpose of this appendix is to show that the set of ensemble-v-representable densities is a dense subset of the set of all N-representable densities. For electron densities that are N-representable, the supremum in Lieb's variational principle exists, i.e.,

$$F_{Legendre}[\rho] \equiv \sup_{v(\boldsymbol{r})} E[v;N] - \int \rho(\boldsymbol{r}) v(\boldsymbol{r}) d\boldsymbol{r} < \infty. \tag{A1}$$

Here, we consider all densities that are non-negative, appropriate normalized, and have finite Weisacker kinetic energy,

$$\infty > \int \frac{\nabla\sqrt{\rho(\boldsymbol{r})}\cdot\nabla\sqrt{\rho(\boldsymbol{r})}}{2}d\boldsymbol{r} \tag{A2}$$

to be N representable. Additional constraints can be imposed if desired. For example, we can restrict ourselves to electron densities that are (essentially) bounded with (essentially) bounded Weisacker kinetic energy densities,

$$\infty > \operatorname*{ess\,sup}_{r} \rho(\boldsymbol{r}),$$

$$\infty > \operatorname*{ess\,sup}_{r} |\nabla\sqrt{\rho(\boldsymbol{r})}|^2, \tag{A3}$$

but this is not required. The essential supremum of a function is the least upper bound, l, such that that bound is exceeded on at most a set of measure zero. We call the set of all allowable densities $\mathcal{D}$ and note that the set of all linear combinations of densities in $\mathcal{D}$ forms a Banach space, $\mathbb{D}$. The space of all bounded linear functionals on $\mathbb{D}$ is denoted $\mathbb{V}\equiv\mathbb{D}^*$, where $\mathbb{D}^*$ indicates the "dual space" of $\mathbb{D}$. The external potentials in the Legendre transform, Eq. (A1), are restricted to the space $\mathbb{V}$.

The norm of an electron density, $\rho(\boldsymbol{r})\in\mathcal{D}\in\mathbb{D}$, is defined as

$$\|\rho(\boldsymbol{r})\|_{\mathbb{D}} \equiv \sup_{\|w\|_{\mathbb{V}}=1}\int w(\boldsymbol{r})\rho(\boldsymbol{r})d\boldsymbol{r}. \tag{A4}$$

Recalling that the supremum is just the least upper bound, the meaning of this expression is clear: the norm of $\rho(\boldsymbol{r})$ is the least upper bound to the expression $\int\rho(\boldsymbol{r})w(\boldsymbol{r})d\boldsymbol{r}$ on the set of all external potentials with unit norm. The norm for external potentials is defined in the same way, but it is important to remember that because $\mathbb{D}$ contains the space of integrable functions, $\mathbb{L}^1$, the dual space of $\mathbb{V}$ is not $\mathbb{D}$. $[\mathbb{V}^*=(\mathbb{D}^*)^*$ contains $\mathbb{D}$, but also includes generalized functions like the Dirac delta function.]

Recalling the definition, Eq. (A1), $F_{Legendre}[\rho]$ is equal to the smallest number, k, for which

$$k \geqslant E[v;N] - \int \rho(\boldsymbol{r})v(\boldsymbol{r})d\boldsymbol{r} \tag{A5}$$

for all external potentials. Suppose that $\rho_t(\boldsymbol{r})$ is a totally non-v-representable density. Then, for any positive number, ε, there must exist an external potential for which

$$F_{Legendre}[\rho_t] - \left(E[v;N] - \int \rho_t(\boldsymbol{r})v(\boldsymbol{r})d\boldsymbol{r}\right) < \varepsilon. \tag{A6}$$

(Otherwise the supremum in Eq. (A1) would be at most $F_{Legendre}[\rho]-\varepsilon$.) Rearranging Eq. (A6) into a form reminiscent of the variational principle gives the key result

Theorem 9. For every $\varepsilon>0$, *there exists a* $v(\boldsymbol{r})\in\mathbb{V}$ *such that*

$$0 < F_{Legendre}[\rho_t] + \int \rho_t(\boldsymbol{r})v(\boldsymbol{r}) - E[v;N] < \varepsilon. \tag{A7}$$

Since ε could be infinitesimal, this indicates that every non-v-representable density gives an "almost perfect" approximation to the ground-state energy for some external potential. Intuitively, this seems to suggest that every non-v-representable electron density would also give an "almost perfect" approximation to the ground state density for some external potential, which would indicate that $\rho_t(\boldsymbol{r})$ was arbitrarily close to some ensemble-v-representable density, which would suffice to demonstrate that the set of ensemble-v-representable densities is a dense subset of the set of "allowed" densities, $\mathcal{D}$.

Confirming this hunch requires two key theorems.

Generalized-Hellmann-Feynman theorem. Let $\mathcal{E}[v]$ *denote the set of ensemble-v-representable densities associated with the ground state of the external potential,* $v(\boldsymbol{r})$. *Because this set consists of weighted sums of the pure-state v-representable densities associated with the (possibly degenerate) ground state of this system,* $\mathcal{E}[v]$ *is a closed, convex set. Consider a small change in the external potential of this state. The resulting change in energy is given by the expression*

$$E[v+\delta v;N] - E[v;N] = \min_{\rho_e(\boldsymbol{r})\in\mathcal{E}[v]}\int \rho_e(\boldsymbol{r})\delta v(\boldsymbol{r})d\boldsymbol{r} + O(\|\delta v(\boldsymbol{r})\|^2). \tag{A8}$$

This theorem will be proved at the conclusion of the appendix, but it is clearly related to the generalization of the Hellmann-Feynman theorem to degenerate states.

Minimum Norm Duality Theorem. Let $\rho_t(\boldsymbol{r})$ *be a distance,* δ, *from the convex set* $\mathcal{E}[v]$. *Then*

$$\delta = \max_{\|w\|_{\mathbb{V}}=1}\int w(\boldsymbol{r})[\rho_t(\boldsymbol{r})-\rho(\boldsymbol{r})]d\boldsymbol{r} \tag{A9}$$

for every $\rho(\boldsymbol{r})\in\mathcal{E}[v]$. *That is, there exists some external potential,* $w(\boldsymbol{r})\in\mathbb{V}$, *with norm one, such that*

$$\int w(\boldsymbol{r})[\rho_t(\boldsymbol{r})-\rho(\boldsymbol{r})]d\boldsymbol{r} \geqslant \delta \tag{A10}$$

for every $\rho(\boldsymbol{r})$ *in* $\mathcal{E}[v]$ [33].

Discussion. The minimum norm duality theorem has a simple geometric interpretation in a Hilbert space. In a Hilbert space, hyperplanes are linear functionals of the form $\hat{\boldsymbol{n}}\cdot\boldsymbol{x}=\alpha$ for some constant α, where $\hat{\boldsymbol{n}}$ is the unit normal to the hyperplane. (The plane goes through the origin if $\alpha=0$; otherwise the plane is shifted from the origin, but parallel to the plane $\hat{\boldsymbol{n}}\cdot\boldsymbol{x}=0$.) There is always a hyperplane that separates a point, $\boldsymbol{x}_t$, that is not in the convex set from the points in the convex set. That is, there is always a unit vector, $\hat{\boldsymbol{n}}_{sep}$, such that

$$\hat{\boldsymbol{n}}_{sep}\cdot\boldsymbol{x} < \hat{\boldsymbol{n}}_{sep}\cdot\boldsymbol{x}_t \quad \forall\ \boldsymbol{x}\in\mathcal{C} \tag{A11}$$

for all $\boldsymbol{x}\in\mathcal{C}$. Usually, in fact, there are many different separating hyperplanes. The minimum norm duality theorem sharpens this result, indicating that if $\boldsymbol{x}_t$ is δ units away from the set $\mathcal{C}$, then at least one of the separating hyperplanes satisfies

$$\hat{\boldsymbol{n}}_{sep} \cdot \boldsymbol{x} + \delta \leqslant \hat{\boldsymbol{n}}_{sep} \cdot \boldsymbol{x}_t \quad \forall \; \boldsymbol{x} \in \mathcal{C}. \tag{A12}$$

This is easily demonstrated. Let $\boldsymbol{x}_{\min}$ be the point in the closure of $\mathcal{C}$ that is closest to $\boldsymbol{x}_t$. (Clearly, $\|\boldsymbol{x}_t - \boldsymbol{x}_{\min}\| = \delta$.) The hyperplane that satisfies Eq. (A12) is just

$$\hat{\boldsymbol{n}}_{sep} \equiv \frac{\boldsymbol{x}_t - \boldsymbol{x}_{\min}}{\|\boldsymbol{x}_t - \boldsymbol{x}_{\min}\|}. \tag{A13}$$

This is quite intuitive since the hyperplane should be normal to the vector that starts at $\boldsymbol{x}_{\min}$ and ends at $\boldsymbol{x}_t$.

The following derivation is essentially a refinement of the intuitive argument presented previously. We will use the fact that every non-v-representable density provides a very accurate approximation to the energy for some external potential to prove that every non-v-representable density can be approximated very accurately by an ensemble-v-representable density.

The proof is by contradiction. If the ensemble-v-representable densities was not dense, then there would exist at least one totally non-v-representable density, $\rho_t(\boldsymbol{r})$, that could not be constructed as a limit of a sequence of ensemble-v-representable densities. Let $\mathcal{E}$ denote the set of ensemble-v-representable densities. If no sequence of densities in $\mathcal{E}$ approached $\rho_t(\boldsymbol{r})$, then the distance between $\rho_t(\boldsymbol{r})$ and the set of ensemble-v-representable densities would be greater than zero. The distance between the $\rho_t(\boldsymbol{r})$ and the set of ensemble-v-representable densities would then be equal to some number $\delta > 0$

$$0 < \delta = d_{\mathbb{D}}(\rho_t, \mathcal{E}). \tag{A14}$$

The distance between $\rho_t(\boldsymbol{r})$ and the set of ensemble-v-representable densities is constructed using the norm in the space $\mathbb{D}$, as

$$d_{\mathbb{D}}(\rho_t, \mathcal{E}) \equiv \inf_{\rho_e \in \mathcal{E}} \|\rho_t(\boldsymbol{r}) - \rho_e(\boldsymbol{r})\|_{\mathbb{D}}. \tag{A15}$$

Choose a small positive number, ε. Then, using the definition of the supremum, there must exist an external potential, $v_\varepsilon(\boldsymbol{r})$, such that $E[v_\varepsilon; N] - \int \rho_t(\boldsymbol{r}) v_\varepsilon(\boldsymbol{r}) d\boldsymbol{r}$ approximates $F_{Legendre}[\rho_t]$ with error less than ε. That is,

$$F_{Legendre}[\rho_t] - \left(E[v_\varepsilon; N] - \int \rho_t(\boldsymbol{r}) v_\varepsilon(\boldsymbol{r}) d\boldsymbol{r} \right) < \varepsilon. \tag{A16}$$

Let $\mathcal{E}[v_\varepsilon]$ denote the set of ensemble-v-representable densities associated with the (possibly degenerate) ground state of the external potential $v_\varepsilon(\boldsymbol{r})$. $\mathcal{E}[v_\varepsilon]$ is a closed, convex set. The distance of $\rho_t(\boldsymbol{r})$ from the set $\mathcal{E}[v_\varepsilon]$ must be at least δ, and so we can use the minimum norm duality theorem to construct an external potential with unit norm, $w_\varepsilon(\boldsymbol{r})$, such that

$$\delta \leqslant \int w_\varepsilon(\boldsymbol{r}) [\rho_t(\boldsymbol{r}) - \rho(\boldsymbol{r})] d\boldsymbol{r} \tag{A17}$$

for every electron density in $\mathcal{E}[v_\varepsilon]$. From the definition of the Legendre-transform functional,

$$F_{Legendre}[\rho_t] \geqslant E[v_\varepsilon - \eta w_\varepsilon; N] - \int \rho_t(\boldsymbol{r}) [v_\varepsilon(\boldsymbol{r}) - \eta w_\varepsilon(\boldsymbol{r})] d\boldsymbol{r}. \tag{A18}$$

From the generalized Hellmann-Feynman theorem,

$$E[v_\varepsilon - \eta w_\varepsilon; N] = E[v_\varepsilon; N] + \min_{\rho_e(\boldsymbol{r}) \in \mathcal{E}[v]} \int \rho_e(\boldsymbol{r}) [-\eta w_\varepsilon(\boldsymbol{r})] d\boldsymbol{r} + O(\eta^2). \tag{A19}$$

Choose η to be small enough so that only the linear term is non-negligible. Then,

$$F_{Legendre}[\rho_t] - \left(E[v_\varepsilon; N] - \int \rho_t(\boldsymbol{r}) v_\varepsilon(\boldsymbol{r}) d\boldsymbol{r} \right) \geqslant \min_{\rho_e(\boldsymbol{r}) \in \mathcal{E}[v]} \int [\rho_e(\boldsymbol{r}) - \rho_t(\boldsymbol{r})][-\eta w_\varepsilon(\boldsymbol{r})] d\boldsymbol{r},$$

$$\varepsilon > \eta \delta. \tag{A20}$$

However, ε can be any arbitrarily small positive number. If $\delta > 0$ is some positive number, then one could always obtain a contradiction to Eq. (A20) by choosing ε to be sufficiently small. From a different perspective, since we can always find a potential for which $\rho_t(\boldsymbol{r})$ approximates the energy arbitrarily closely, we can take the limit of the first line of Eq. (A20) as $\varepsilon \to 0$. This forces the limit of the second line, which related to the distance of $\rho_t(\boldsymbol{r})$ from the set of ensemble-v-representable densities, to also approach zero. This is exactly the construction anticipated at the beginning of this appendix: the fact that $\rho_t(\boldsymbol{r})$ approximates the energy very accurately for some external potential means that there must be some ensemble-v-representable density that approximates $\rho_t(\boldsymbol{r})$ very accurately.

To conclude this appendix, the generalized Hellmann-Feynman theorem used in the preceding derivation is derived.

The Generalized Hellmann-Feynman Theorem. Recall the equations for the v-representable densities associated with a degenerate state [cf. Eqs. (6) and (7)]. Again, letting $\{\psi_i\}_{i=1}^{g}$ denote any orthonormal basis for the wave functions of the degenerate ground state, all of the v-representable densities can be written in the form

$$\rho_v^{(n)}(\boldsymbol{r}) = \sum_{i=1}^{g} \sum_{j=1}^{g} (k_i^{(n)})^* k_j^{(n)} \langle \psi_i | \hat{\rho}(\boldsymbol{r}) | \psi_j \rangle, \tag{A21}$$

where

$$\sum_{i=1}^{g} |k_i|^2 = 1. \tag{A22}$$

We denote the pure-state v-representable densities associated with the external potential $v(\boldsymbol{r})$ as $\mathcal{V}[v]$. It is useful to rephrase Eqs. (A21) and (A22) as

$$\rho_v(\boldsymbol{r}) = \sum_{i=1}^{g} \sum_{j=1}^{g} c_{ij} \langle \psi_i | \hat{\rho}(\boldsymbol{r}) | \psi_j \rangle, \tag{A23}$$

where it is understood that

$$0 \leqslant c_{ii} \leqslant 1, \tag{A24}$$

$$\sum_{i=1}^{g} c_{ii} = 1, \tag{A25}$$

$$c_{ij} = c_{ji}^{*}, \tag{A26}$$

$$|c_{ij}|^2 = c_{ii} c_{jj}. \tag{A27}$$

The set of ensemble-v-representable densities associated with the external potential $v(\boldsymbol{r})$, denoted $\mathcal{E}[v]$, is by definition the convex closure of the set of pure-state v-representable densties, $\mathcal{V}[v]$. Thus, the ensemble-v-representable densities, $\rho_e(\boldsymbol{r}) \in \mathcal{E}[v]$, can be written as

$$\rho_e(\boldsymbol{r}) = \sum_{i=1}^{g} \sum_{j=1}^{g} c_{ij} \langle \psi_i | \hat{\rho}(\boldsymbol{r}) | \psi_j \rangle, \tag{A28}$$

where the constraints (A24)–(A26) still hold, but Eq. (A27) is replaced by the inequality

$$|c_{ij}|^2 \leqslant c_{ii} c_{jj}. \tag{A29}$$

$\mathcal{E}[v]$ is a closed convex set, and $\mathcal{V}[v]$ is its boundary.

For a nondegenerate state, one has that

$$E[v + \delta v ; N] - E[v ; N] = \int \rho_v(\boldsymbol{r}) \delta v(\boldsymbol{r}) d\boldsymbol{r} + O(\|\delta v(\boldsymbol{r})\|^2), \tag{A30}$$

where $\rho_v(\boldsymbol{r})$ is the ground state density of the state. Equation (A30) is just the Hellmann-Feynman theorem.

For a degenerate state, the ground state energy is given by the lowest eigenvalue of the perturbation matrix,

$$V_{pq} = \langle \psi_q | \sum_{i=1}^{N} \delta v(\boldsymbol{r}_i) | \psi_p \rangle \tag{A31}$$

which can be found as

$$\begin{aligned} &E[v + \delta v ; N] - E[v ; N] \\ &\quad = \min_{\{k_p\}_{p=1}^{g}} \left\langle \sum_{q=1}^{g} k_q \psi_q \middle| \sum_{i=1}^{N} \delta v(\boldsymbol{r}_i) \middle| \sum_{p=1}^{g} k_p \psi_p \right\rangle + O(\|\delta v(\boldsymbol{r})\|^2) \end{aligned} \tag{A32}$$

or, equivalently, as

$$\begin{aligned} E[v + \delta v ; N] - E[v ; N] = \min_{\rho_v(\boldsymbol{r}) \in \mathcal{V}[v]} \int \rho_v(\boldsymbol{r}) \delta v(\boldsymbol{r}) d\boldsymbol{r} \\ + O(\|\delta v(\boldsymbol{r})\|^2) \end{aligned} \tag{A33}$$

or even

$$\begin{aligned} E[v + \delta v ; N] - E[v ; N] = \min_{\rho_e(\boldsymbol{r}) \in \mathcal{E}[v]} \int \rho_e(\boldsymbol{r}) \delta v(\boldsymbol{r}) d\boldsymbol{r} \\ + O(\|\delta v(\boldsymbol{r})\|^2). \end{aligned} \tag{A34}$$

The last equality follows uses the fact that $\mathcal{E}[v]$ is the convex closure of $\mathcal{V}[v]$. Equation (A34) is the "generalized Hellmann-Feynman theorem" relevant in this appendix.

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[21] See theorem 8 and the surrounding discussion for a derivation of this result.

[22] There is significant flexibility in how one chooses the norm of the density and the norm of the potential. The key is that the potential lies in the dual space to the density, so that the two norms are "paired." Thus, if one adds additional restrictions on the density (for example, one might require that the density be not only integrable, but bounded), then one will widen the class of possible external potentials. In all cases, the normal-

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[30] Strictly speaking, this is only true for so-called "conventional" density variations (see Ref. [14]). However, for unconventional variations, the change in F due to a change in density is still proportional to the to the change in density (plus smaller quadratic terms), and so the right-hand side of Eq. (34) still becomes negligible as k approaches infinity. Thus, while Eq. (35) does not hold for "unconventional" density variations, the key limit still exists and is well behaved.
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