PHYSICAL REVIEW A **80**, 032510 (2009)

Density-functional theory with additional basic variables: Extended Legendre transform

Paul W. Ayers[1] and Patricio Fuentealba[2]
[1]*Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1*
[2]*Department of Physics, Faculty of Science, University of Chile, 653-Santiago, Chile*

(Received 27 February 2009; published 14 September 2009)

In a recent series of papers, Higuchi and Higuchi defined an extended constrained-search procedure by extending the Levy constrained search by adding additional constraints. As shown here, this procedure can be equivalently formulated in terms of Lieb's Legendre transformation functional. The Legendre transform approach has advantages in cases where the additional constraints are restrictive enough to cause problems with N-representability.

DOI: 10.1103/PhysRevA.80.032510   PACS number(s): 31.15.E−

I. BACKGROUND AND MOTIVATION

A. Density-functional theory

Since the fundamental importance of electronic structure for understanding the properties of molecules and materials was recognized even before Rutherford's work on the structure of the atom, it is almost surprising that the quantum-mechanical theory of electronic structure is still an active subject of research. Part of the problem is the enormous complexity of describing electron correlation in many-electron systems. It is simply impossible to write a quantitatively accurate approximation to the N-electron wave function for a system with more than a few electrons. Instead, one either chooses a parametrization for the wave function that reduces the number of degrees of freedom or one opts to consider only a subset of the electronic coordinates and then uses the fact that electrons are identical particles to infer the properties of the implicit "other electrons."

Density-functional theory (DFT) is among the simplest of the "reduced" electronic structure theories. According to the theorem of Hohenberg and Kohn, if we know the electron density $\rho(\mathbf{r})$, then we can determine all of the properties of any electronic system, including the ground-state energy. The ground-state energy is, following Hohenberg and Kohn, determined by a variational principle for minimizing the energy with respect to all electron densities that are non-negative and normalized to the number of electrons, i.e., [1]

$$E_{gs}[v;N] = \underbrace{\min}_{\substack{\rho(\mathbf{r})\geq 0\\ \langle\rho\rangle=N}} \left\{ F[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \right\}. \tag{1}$$

Here, $F[\rho]$ is the sum of the kinetic and the electron-electron repulsion energies. The second term in the energy expression is the interaction energy of the electrons with the external potential due to the atomic nuclei (and an external electric field, if that is also present).

B. v- and N-representability problems

DFT is intuitively simple but mathematically subtle. It is relatively easy to define the Hohenberg-Kohn functional

$$F[\rho_{gs}] = E_{gs}[v;N] - \int \rho_{gs}(\mathbf{r})v(\mathbf{r})d\mathbf{r} \tag{2}$$

for electron densities that are the N-electron ground state for some external potential. Unfortunately, not every electron density is v-representable. In fact, the set of non-v-representable electron densities is a dense subset of the domain of the variational principle (1) [2–5]. This makes it difficult to implement the variational principle.

There are several ways to avoid this problem. First of all, one can solve a problem in the dual space, where the potential is the variable instead of the electron density [6,7]. Second, one can take the definition in Eq. (2) and use mathematical arguments based on continuity to define a functional over the entire variational domain [5]. These approaches are mathematically appropriate, but perhaps conceptually unsatisfactory: they avoid the issue of how to define $F[\rho]$ for non-v-representable densities. This is one reason that most of the work in density-functional theory is based on one of the two ways to define the Hohenberg-Kohn functional. One approach, originally due to Levy and Perdew [8,9] (later extended by Valone [10] and explored by Lieb [11] and others [12]) is the constrained search, where one minimizes the sum of the kinetic and the electron-electron repulsion energies with respect to every wave function that gives a specified electron density

$$F_{cs}[\rho] = \underbrace{\min}_{\Psi\to\rho(\mathbf{r})} \langle\Psi|\hat{T}+V_{ee}|\Psi\rangle. \tag{3}$$

Another approach, due to Lieb, is the Legendre transform

$$F_{Leg}[\rho] = \underbrace{\sup}_{v(\mathbf{r})} \left\{ E_{gs}[v;N] - \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \right\}. \tag{4}$$

Both approaches are mathematically rigorous [11] and the current consensus seems to be that the constrained search is more useful for determining constraints on the exact functional, while the Legendre transform approach is more useful for formal work.

One issue that arises in the context of the constrained-search functional is the problem of N-representability. The constrained-search functional is not defined unless there exists some wave function with the specified density $\rho(\mathbf{r})$. Fortunately for any electron density that satisfies the constraints in the variational principle (that is, every electron density that is non-negative and normalized to the number of electrons), there always exists a wave function such that [13,14]

$$\rho(\mathbf{r}) = \langle \Psi | \sum_{i=1}^{N} \delta(\mathbf{r}_i - \mathbf{r}) | \Psi \rangle. \tag{5}$$

(Not only that, but there exists a Slater determinant with this electron density.) This proves that every "reasonable" electron density is N-representable.

C. Generalized density-functional theories

Recently there has been significant interest in what might be termed "generalized" density-functional theories. Some workers have attempted to model electronic systems using alternatives to the electron density [15–17], some of which are even simpler (e.g., the density per particle [18–20]) than the electron density. While this approach seems to be useful for describing the similarity of different molecules and materials, it does not appear to give a quantitatively accurate variational principle [21]. An alternative approach is to consider descriptors of electronic structure that contain more information than the electron density. Some of these theories are very well known (e.g., density-functional theory using the spin densities [22–24] or both the density and the current density [25,26]). Variational methods based on the first-order reduced density matrix [8,13,27], the higher-order reduced density matrices [28–32], the electron pair density [33–43], the higher-order electron distribution functions, [37,38] the "polydensities" of various types [44–49], or the electron propagator [50,51] can also be considered as generalized density-functional theories [52,53], since all of these quantities contain information about the electron density (and more besides).

In a recent series of papers, Higuchi and Higuchi present a family of "extended" density-functional theories that use more information than the "traditional" extended density-functional theories used to describe magnetic systems but less information than the generalized density-functional theories used to provide an improved description of electron correlation [54–58]. In particular, they define an extended constrained-search functional

$$F_X^{\text{xCS}}[\rho] = \underbrace{\min}_{\Psi \to \rho, \mathbf{X}} \langle \Psi | \hat{T} + V_{ee} | \Psi \rangle, \tag{6}$$

where the usual restriction that the wave function gives the desired electron density ($\Psi \to \rho$) is now supplemented by the additional restriction that the wave function gives the desired expectation value for some additional property (or properties) ($\Psi \to \mathbf{X}$). If one chooses the spin density or the paramagnetic current density as the supplementary property [54,56], then one obtains a constrained-search formulation of spin-DFT or spin-current-DFT (although there are formal difficulties in the latter case, the Hohenberg-Kohn theorem fails because different magnetic Hamiltonians can have the same ground-state wave function [6,23,59–66]). Note that our notation differs slightly from Higuchi and Higuchi's who would write $F^{\text{xCS}}[\rho,\mathbf{X}]$ instead of $F_{\mathbf{X}}^{\text{xCS}}[\rho]$. Our notation seems more appropriate in cases where the property $\mathbf{X}$ is determined by the system of interest and is not varied during the variational minimization of the energy functional.

Higuchi and Higuchi's extended constrained search (6) provides a powerful method for deriving generalized density-functional theories as long as there exists some wave function with the specified electron density $\rho(\mathbf{r})$ and properties $\mathbf{X}$. That is, the extended constrained search is defined if $\{\rho,\mathbf{X}\}$ is N-representable, but not otherwise. Higuchi and Higuchi deal with this by *assuming* that $\{\rho,\mathbf{X}\}$ is N-representable. This is satisfactory from a mathematical point of view but perhaps not from a practical point of view: it is usually very difficult to find computationally facile N-representability conditions. (The electron density and the spin-density are well-known exceptions.)

The problem is well known in the other generalized density-functional theories discussed above and, indeed, all of those theories can be treated with special cases of the extended constrained search. The N-representability problem also arises in other circumstances, however. For example, in their second paper Higuchi and Higuchi propose a type of Hartree-Fock Kohn-Sham theory [54,67–69]

$$F_{E_x}^{\text{xCS}}[\rho] = \underbrace{\min}_{\Psi \to \rho, E_x} \langle \Psi | \hat{T} + V_{ee} | \Psi \rangle. \tag{7}$$

Not every pairing of electron density and exchange energy is N-representable, however [70–73]. Every electron density corresponds to a set of Slater determinants, and these Slater determinants determine, in turn, a range of reasonable (i.e., N-representable) exchange energies associated with this electron density. Not every choice of the exchange energy is reasonable. Clearly $E_x \leq 0$, but there is also a density-dependent lower bound on the range of N-representable exchange energies. This follows from the Lieb-Oxford bound [74–76], which indicates that the exchange-correlation energy should always be greater than

$$E_x[\rho] \geq E_{xc}[\rho] \geq E_{xc}^{(\text{LO})}[\rho],$$

$$E_{xc}^{(\text{LO})}[\rho] \equiv -1.6358 \int \rho^{4/3}(\mathbf{r}) d\mathbf{r}. \tag{8}$$

One cannot perform the extended constrained search for $\{\rho(\mathbf{r}), E_x^{(\text{trial})}\}$ if $E_x^{(\text{trial})} > 0$ or $E_x^{(\text{trial})} < E_x^{(\text{LO})}[\rho]$. Unfortunately, the Lieb-Oxford bound is not very tight [74,77], so it is insufficient for constraining the domain of the constrained search in Eq. (7). The exact N-representability bound can be derived using the general formalism in Ref. [70], but it is too complicated to be computationally facile: it is easier to compute the value of E_x exactly.

Higuchi and Higuchi also presented approaches to the pair-density–functional theory using the extended constrained search [41,42,78,79]. The N-representability problem for the pair density is known to be very difficult [38,80–84] (although it can be surmounted using either conventional constrained-search [53] or Legendre transform methods [38,52,53]). In order to circumvent these difficulties, Higuchi and Higuchi are forced to restrict their search to pair densities for which they can explicitly reconstruct the precursor wave functions, e.g., Slater determinants or Jastrow-type wave functions [85,86]. This gives a practical approach to pair-DFT, albeit one that is limited by the imperfections in the simplified forms of the wave functions being considered. Already in their first paper, Higuchi and Higuchi showed that the N-representability problem for other choices of $\mathbf{X}$ can be attacked in the same way, by restricting oneself choices of $\mathbf{X}$ and $\rho(\mathbf{r})$ that can be produced by Slater determinants [56]. One advantage of this approach is that it gives a set of single-particle equations to solve [56]. The disadvantage, already noted above, is that the set of $\{\rho,\mathbf{X}\}$ that is obtainable from Slater determinant wave functions typically contains only a small portion of the space of all possible pairings between $\mathbf{X}$ and $\rho(\mathbf{r})$ [87]. In particular, the true ground-state values for $\mathbf{X}$ and $\rho(\mathbf{r})$ may not be Slater-N-representable. It would be better if there were a way to attack the N-representability issue directly.

By this stage, the reader is hopefully convinced that N-representability issues are a big—and perhaps insurmountable—problem for the extended constrained-search procedure. This problem is known in the context of other generalized density-functional theories, and two solutions have been proposed. The first approach is a “weak constrained search” where one relaxes the assumption that the wave function must give *exactly* the correct property value and then compensates for this flexibility with an appropriate penalty term [53]. The second approach is based on the Legendre transform [52,53] and requires inserting a “dual variable” conjugate to the property being optimized. (The dual variable is just a Lagrange multiplier.) In the next section of this paper, we will show how the Legendre transform approach addresses the N-representability problem in extended density-functional theories of the Higuchi-Higuchi type. A short summary will then conclude the analysis. Key theorems are proved in the Appendix.

II. EXTENDED LEGENDRE TRANSFORM

A. Partial Legendre transform

There are three forms of the Legendre transform that will be considered in this work. First of all, one can perform a “partial Legendre transform” with respect to only the electron density

$$F_{\mathbf{X}}[\rho] = \underbrace{\sup}_{v(\mathbf{r})} \left\{ E_{gs}[v,\mathbf{X};N] - \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \right\}. \tag{9}$$

The expression for the ground-state energy expression that enters into Eq. (9) is defined by

$$E_{gs}[v,\mathbf{X};N] = \underbrace{\min}_{\left\{\Psi \middle| {\Psi \ \text{anti.},\langle\Psi|\Psi\rangle=1 \atop \Psi\to N,\mathbf{X}}\right\}} \langle \Psi | \hat{T} + V_{ee} + \sum_{i=1}^{N} v(\mathbf{r}_i) | \Psi \rangle. \tag{10}$$

The corresponding energy density functional and its variational principle are

$$\mathcal{E}_{v,\mathbf{X}}[\rho] = F_{\mathbf{X}}[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \geq E_{gs}[v,\mathbf{X},N]. \tag{11}$$

The variational inequality holds for every choice of the electron density, even if there does not exist any wave function with that density that also has the property value $\mathbf{X}$. (However, in order to define the energy functional in Eq. (10), there must be a wave function that has property value $\mathbf{X}$, even though this wave function may not have the targeted density.) Notice that $E_{gs}[v,\mathbf{X};N]$ is the lowest-energy state of the system with property value $\mathbf{X}$; it is only equal to the true ground-state energy if $\mathbf{X}$ is chosen as the property value in the ground state. By choosing $\mathbf{X}$ to have non-ground-state values, one obtains energetic information about select excited states.

When the supremum in Eq. (9) is a maximum, the electron density is the ground-state density, with property $\mathbf{X}$, for the maximizing potential $v_{\max}(\mathbf{r})$. This establishes an $\mathbf{X}$-dependent mapping between the electron density and the external potential.

This partial Legendre transform is very useful when $\mathbf{X}$ is a property (e.g., a specific choice of spatial symmetry or spin multiplicity) of the state of interest and we do not want to optimize with respect to that variable. Lieb’s Legendre transform is actually a special case of this form, because in that case the number of electrons, N, is fixed. (That assumption can be relaxed, of course, using the form of the energy for arbitrary electron number [88–90].)

B. Full Legendre transform

Second, one can perform a “full Legendre transform” with respect to both variables. When $\mathbf{X}$ is the expectation value of a linear operator related to a term in the Hamiltonian, then matters are especially simple, and one has

$$F[\rho,\mathbf{X}] = \underbrace{\sup}_{v(\mathbf{r}),\mathcal{X}} \left\{ E_{gs}[v,\mathcal{X};N] - \langle \mathcal{X},\mathbf{X}\rangle - \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \right\}. \tag{12}$$

The quantity $\mathcal{X}$ is the dual variable to $\mathbf{X}$,

$$\mathbf{X} = \frac{\delta E_{gs}[v,\mathcal{X},N]}{\delta \mathcal{X}}, \tag{13}$$

and enters Eq. (12) as a Lagrange multiplier for forcing the property $\mathbf{X}$ to have the desired value. The notation $\langle \mathcal{X},\mathbf{X}\rangle$ is the inner product between $\mathbf{X}$ and its dual vector. When $\mathbf{X}$ is a scalar (e.g., the exchange energy), $\langle \mathcal{X},\mathbf{X}\rangle$ is simple multiplication. When $\mathbf{X}$ is a vector (e.g., the number of electrons of each spin, $[N_\alpha,N_\beta]$), $\langle \mathcal{X},\mathbf{X}\rangle$ is a dot product. When $\mathbf{X}$ is a function (or vector of functions) [e.g., the magnetization density $m(\mathbf{r})$], $\langle \mathcal{X},\mathbf{X}\rangle$ is multiplication (or dot product) followed by integration. [For example, for the magnetization density, $\langle \mathcal{X},\mathbf{X}\rangle \to \langle \mu B_z(\mathbf{r}), m(\mathbf{r})\rangle = \int \mu B_z(\mathbf{r}) m(\mathbf{r}) d\mathbf{r}$.]

The expression for the ground-state energy expression that enters into Eq. (12) is defined by

$$E_{gs}[v,\mathcal{X},N] = \underbrace{\min}_{\left\{\Psi\middle|\substack{\Psi\ \text{anti.},\langle\Psi|\Psi\rangle=1\\ \Psi\to N}\right\}} \langle\Psi|\hat{T}+V_{ee}+\sum_{i=1}^{N}v(\mathbf{r}_i)|\Psi\rangle+\langle\mathcal{X},\mathbf{X}[\Psi]\rangle. \tag{14}$$

In the important case where there is a linear operator

$$\mathbf{X}[\Psi]=\langle\Psi|\hat{\mathcal{X}}|\Psi\rangle, \tag{15}$$

then $\langle\mathcal{X},\mathbf{X}[\Psi]\rangle$ can be re-expressed as a linear operator on the wave function $\langle\Psi|\hat{\mathcal{X}}|\Psi\rangle$ and the last term in Eq. (14) can be incorporated into the main energy expression, giving

$$E_{gs}[v,\mathcal{X},N] = \underbrace{\min}_{\left\{\Psi\middle|\substack{\Psi\ \text{anti.},\langle\Psi|\Psi\rangle=1\\ \Psi\to N}\right\}} \langle\Psi|\hat{T}+V_{ee}+\hat{\mathcal{X}}+\sum_{i=1}^{N}v(\mathbf{r}_i)|\Psi\rangle. \tag{16}$$

The corresponding energy functional and its variational principle are

$$\mathcal{E}_{v,\mathcal{X}}[\rho,\mathbf{X}] \equiv F[\rho,\mathbf{X}] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + \langle\mathcal{X},\mathbf{X}\rangle,$$

$$\mathcal{E}_{v,\mathcal{X}}[\rho,\mathbf{X}] \geq E_{gs}[v,\mathcal{X},N]. \tag{17}$$

The variational inequality holds for every choice of the electron density, even if there does not exist any wave function with that density that also has the property value **X**. Notice that the term $\langle\mathcal{X},\mathbf{X}\rangle$ corresponds to an additional term in the Hamiltonian. Sometimes this term is physically relevant [recall that $\mathcal{X}=\mu B_z(\mathbf{r})$ in spin-density functional theory], but often it is not. The presence of the additional term causes no problems, however: the "conventional" energy is computed using the special case of Eqs. (17) where $\mathcal{X}=0$.

Examples of full Legendre transforms include the average-pair density-functional theory of Gori-Giorgi and Savin [46,48,91], spin-density functional theory [92,93], and current density-functional theory [25,26]. Another example arises when **X** is the number of electrons, in which case Eq. (12) recovers the grand canonical formulation of density-functional theory [88,94,95].

C. Restricted Legendre transform

Finally, the outer supremum in either Eq. (9) or Eq. (12) can be restricted when only special classes of systems are of interest [52]. For example, one can restrict the external potentials to just the Coulombic forms

$$v(\mathbf{r}) = -\sum_{\eta}\frac{q_\eta}{|\mathbf{r}-\mathbf{R}_\eta|} \tag{18}$$

or even only molecular forms (where all of q_η are integers). This sort of formulation is useful in alchemical transformations [96–101] and provides links to the "less than density" generalized density-functional theories [16–18]. In addition, one can choose to restrict the search over the property potential $\mathcal{X}$ in the full Legendre transform (12). For example, often the only physically reasonable choice is $\mathcal{X}=0$.

When the supremization is restricted to a subset of the values of $\{v(\mathbf{r}),\mathcal{X}\}$ that are allowed by functional analysis, we call the functional a "restricted Legendre transform." Clearly the restricted Legendre transform functionals are lower bounds to the corresponding unrestricted Legendre transform functionals. The corresponding functionals and variational principles are exact for systems whose external potential has the special form [e.g., Eq. (18)] used in the restricted functional. Otherwise, the functional gives a lower bound (albeit sometimes a tight lower bound) on the energy. The advantage of restricted functionals is that, by restricting ourselves to systems of physical relevance, we obtain functionals that are smaller, ergo mathematically "nicer."

D. Properties of the functionals

These formulations have several key properties, which are proved in the Appendix. Chief among them are

(1) The suprema are unique.

(2) The functionals are exact.

(3) The variational principle holds, even when $\{\rho(\mathbf{r}),\mathbf{X}\}$ is not *N*-representable.

(4) The functionals are convex, and so the minimum is unique.

(5) The unrestricted functionals are infinity for non-*N*-representable cases.

(6) The partial Legendre transform functional is an upper bound to the full Legendre transform functional.

(7) The extended constrained-search functional is an upper bound to the partial Legendre transform functional.

Properties (1)–(5) were established by Lieb for the conventional DFT Legendre transform [11] and by Ayers *et al.* for some special cases of the full Legendre transform [52]. The partial Legendre transform [Eq. (9)] is very similar to the conventional Lieb Legendre transform, while the full Legendre transform [Eq. (12)] is very similar to the Ayers-Golden-Levy Legendre transform. We merely extend these derivations here.

The derivation of properties (6) and (7) is similar to the argument that the value of the Levy constrained-search functional is greater than or equal to the value of the Legendre transform functional [9,11]: the key to deriving property (6) is to notice that the partial Legendre transform includes a "constrained search" over wave functions restricted to have property **X**, while the full Legendre transform does not. Properties (1)–(7) are derived in the Appendix. Since the derivations for the full Legendre transform functional are the most challenging, the Appendix focuses on that functional.

III. SUMMARY

In analogy to the "extended constrained-search" functionals of Higuchi and Higuchi [54–56], the functionals defined in Secs. II A–II C can be considered as "extended Legendre transform" functionals. These functionals are useful for extending density-functional theory to cases where not only the electron density $\rho(\mathbf{r})$, but also some property of the system, **X**, is of interest. This is particularly important when one wishes to consider only wave functions with a specific property, like a specified symmetry. The extended constrained-search and extended Legendre transform functionals are identical for densities that are $\{v(\mathbf{r}),\mathcal{X}\}$-representable, but in general the Legendre transform functionals are a lower bound to the constrained-search functionals. Importantly, the Legendre transform functionals are defined even when $\{\rho(\mathbf{r}),\mathbf{X}\}$ is not N-representable, that is, when there is no wave function with density $\rho(\mathbf{r})$ and property value $\mathbf{X}$.

We proposed three different forms of Legendre transform functionals. The first, $F_{\mathbf{X}}[\rho]$, is what we call the "partial" Legendre transform: it corresponds to the Legendre transform of the energy functional, $E[v,\mathbf{X},N]$ [cf. Eq. (10)] with respect to the external potential $v(\mathbf{r})$. The second functional $F[\rho,\mathbf{X}]$ is the Legendre transform of $F_{\mathbf{X}}[\rho]$ with respect to $\mathbf{X}$. Both of these functionals can be "restricted" by including only certain classes of external potentials in the supremum [cf. Eqs. (9) and (12)]. The restricted functionals have the advantage of being better behaved [especially for non-N-representable $\{\rho(\mathbf{r}),\mathbf{X}\}$], but are only exact for systems with external potentials that are included in the supremization procedure. We have the general inequalities $F^{\text{restricted}}[\rho,\mathbf{X}] \le F[\rho,\mathbf{X}] \le F_{\mathbf{X}}[\rho] \le F_{\mathbf{X}}^{\text{xCS}}[\rho]$, where $F_{\mathbf{X}}^{\text{xCS}}[\rho]$ is the extended constrained-search functional of Higuchi and Higuchi in Eq. (6). However, the extended constrained-search functional is not defined for all possible densities $\rho(\mathbf{r})$ and property values $\mathbf{X}$. The partial Legendre transform is defined for all densities, as long as there exists at least one wave function with property value $\mathbf{X}$. (For example, the exact-exchange partial Legendre transform $F_{E_x}[\rho]$ is undefined for $E_x>0$. Similarly, the total-spin partial Legendre transform $F_S[\rho]$ is undefined for $S<0$.) The full Legendre transform is defined for all densities $\rho(\mathbf{r})$ and all property values $\mathbf{X}$, whether or not they are physical. For this reason the full Legendre transform seems more useful in cases where it is difficult to assess whether a property density is reasonable or not. (A good example is average-pair DFT [46,48,91], where the N-representability problem is distinctly nontrivial.) Both the partial Legendre transform and the full Legendre transform become infinity when there is no wave function consistent with their argument. The restricted Legendre transform usually does not suffer from this divergence, and it is still exact for all systems whose external potentials are included in the domain of the search. The restricted functionals are lower bounds to the true energy for other systems.

Replacing the electron-electron repulsion operator V_{ee} with λV_{ee} in any of these functionals allows one to formulate the adiabatic connection from the noninteracting (extended Kohn-Sham) to the interacting system. Then, in the standard way [58,102–106], each of the extended Legendre transform functionals defines the functionals and potentials to be used with single-particle Kohn-Sham-like equations, analogous to those derived previously using the extended constrained-search approach [56,58].

ACKNOWLEDGMENTS

P.W.A. acknowledges support from NSERC, the Canada Research Chairs, Sharcnet, and the Alfred P. Sloan Foundation. P.F. acknowledges support from FONDECYT Grant No. 1080184.

APPENDIX

In this appendix we will focus on the total Legendre transform functional [Eq. (12)] because the analogous results for the other functionals are similar, but usually easier.

(1) Suprema are unique. The supremum in Eq. (12) is unique because its argument

$$F_{\rho,\mathbf{X}}[v,\mathcal{X},N] = E_{gs}[v,\mathcal{X};N] - \langle \mathcal{X},\mathbf{X}\rangle - \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \quad \text{(A1)}$$

is a concave functional of $v(\mathbf{r})$ and $\mathcal{X}$, i.e., the weighted average of the functional for two arguments is less than the value of the functional at the weighted average of its arguments,

$$\begin{aligned} &F_{\rho,\mathbf{X}}[tv_1+(1-t)v_2,t\mathcal{X}_1+(1-t)\mathcal{X}_2,N] \\ &\quad \ge tF_{\rho,\mathbf{X}}[v_1,\mathcal{X}_1,N]+(1-t)F_{\rho,\mathbf{X}}[v_2,\mathcal{X}_2,N]. \end{aligned} \quad \text{(A2)}$$

$F_{\rho,\mathbf{X}}[v,\mathcal{X},N]$ is a concave functional because it is a sum of a concave functional ($E_{gs}[v,\mathcal{X};N]$) and a linear functional. $E_{gs}[v,\mathcal{X};N]$ is concave because, by the variational principle,

$$\begin{aligned} &E_{gs}[tv_1+(1-t)v_2,t\mathcal{X}_1+(1-t)\mathcal{X}_2,N] \\ &= \underbrace{\min}_{\left\{\Psi \middle| \substack{\Psi\ \text{anti.},\langle\Psi|\Psi\rangle=1 \\ \Psi\to N}\right\}} \Bigg(\langle\Psi| t\left(\hat{T}+V_{ee}+\sum_{i=1}^{N} v_1(\mathbf{r}_i)\right) \\ &\quad + (1-t)\left(\hat{T}+V_{ee}+\sum_{i=1}^{N} v_2(\mathbf{r}_i)\right)|\Psi\rangle + t\langle\mathcal{X}_1,\mathbf{X}[\Psi]\rangle \\ &\quad + (1-t)\langle\mathcal{X}_2,\mathbf{X}[\Psi]\rangle \Bigg) \\ &\ge \underbrace{\min}_{\left\{\Psi \middle| \substack{\Psi\ \text{anti.},\langle\Psi|\Psi\rangle=1 \\ \Psi\to N}\right\}} t\Bigg(\langle\Psi|\hat{T}+V_{ee}+\sum_{i=1}^{N} v_1(\mathbf{r}_i)|\Psi\rangle \\ &\quad + \langle\mathcal{X}_1,\mathbf{X}[\Psi]\rangle \Bigg) + \underbrace{\min}_{\left\{\Psi \middle| \substack{\Psi\ \text{anti.},\langle\Psi|\Psi\rangle=1 \\ \Psi\to N}\right\}} (1-t)\Bigg(\langle\Psi|\hat{T}+V_{ee} \\ &\quad + \sum_{i=1}^{N} v_2(\mathbf{r}_i)|\Psi\rangle + \langle\mathcal{X}_2,\mathbf{X}[\Psi]\rangle \Bigg) \\ &= tE_{gs}[v_1,\mathcal{X}_1,N]+(1-t)E_{gs}[v_2,\mathcal{X}_2,N]. \end{aligned} \quad \text{(A3)}$$

The inequality follows from the fact that the minimum of a sum is greater than the sum of the minima. A more detailed discussion of this argument can be found in Ref. [92]; see especially footnote 26.

The supremum of a concave functional is unique. This means that every choice of $\{\rho(\mathbf{r}),\mathbf{X}\}$ is assigned to a specific value of

$$F[\rho,\mathbf{X}] = \underbrace{\sup}_{v,\mathcal{X}} F_{\rho,\mathbf{X}}[v,\mathcal{X},N] \quad \text{(A4)}$$

and that there are no local maxima that could complicate this optimization. Moreover, if there exists some $\{v_{\max}(\mathbf{r}),\mathcal{X}_{\max}\}$ such that $F[\rho,\mathbf{X}]=F_{\rho,\mathbf{X}}[v_{\max},\mathcal{X}_{\max},N]$ (i.e., the supremum is actually a maximum), then Eq. (A4) provides a unique mapping between $\{\rho(\mathbf{r}),\mathbf{X}\}$ and $\{v_{\max}(\mathbf{r}),\mathcal{X}_{\max}\}$. This is an extended Hohenberg-Kohn theorem: there cannot be two pairs $\{v^{(1)}_{\max}(\mathbf{r}),\mathcal{X}^{(1)}_{\max}\}$ and $\{v^{(2)}_{\max}(\mathbf{r}),\mathcal{X}^{(2)}_{\max}\}$ (differing by more than an arbitrary constant) that have the same ground state $\{\rho(\mathbf{r}),\mathbf{X}\}$.

The derivation for the partial Legendre transform $F_{\mathbf{X}}[\rho]$ is similar, but even simpler. The key results still hold, but now the extended Hohenberg-Kohn theorem establishes that there cannot be two external potentials, differing by more than an additive constant, with the same ground state $\{\rho(\mathbf{r}),\mathbf{X}\}$.

(2) The functionals are exact. Suppose that one is given two different systems in their electronic ground state:

$$\begin{aligned}&\{\rho_1(\mathbf{r}),\mathbf{X}_1\}\rightarrow\{v_1(\mathbf{r}),\mathcal{X}_1\},\\ &\{\rho_2(\mathbf{r}),\mathbf{X}_2\}\rightarrow\{v_2(\mathbf{r}),\mathcal{X}_2\}.\end{aligned}\tag{A5}$$

Denote the ground-state wave functions for these systems as Ψ_1 and Ψ_2, respectively. Then, from the variational principle for the energy [cf. Eq. (14)],

$$E_{gs}[v_1,\mathcal{X}_1,N]\le\langle\Psi_2|\hat{T}+V_{ee}+\sum_{i=1}^{N}v_1(\mathbf{r}_i)|\Psi_2\rangle+\langle\mathcal{X}_1,\mathbf{X}[\Psi_2]\rangle,$$

$$\begin{aligned}E_{gs}[v_1,\mathcal{X}_1,N]-\langle\mathcal{X}_1,\mathbf{X}_2\rangle-\int\rho_2(\mathbf{r})v_1(\mathbf{r})d\mathbf{r}\\ \le E_{gs}[v_2,\mathcal{X}_2,N]-\langle\mathcal{X}_2,\mathbf{X}_2\rangle\\ -\int\rho_2(\mathbf{r})v_2(\mathbf{r})d\mathbf{r},\end{aligned}$$

$$F_{\rho_2,\mathbf{X}_2}[v_1,\mathcal{X}_1,N]\le F_{\rho_2,\mathbf{X}_2}[v_2,\mathcal{X}_2,N].\tag{A6}$$

The equality holds only if $\{v_1(\mathbf{r}),\mathcal{X}_1\}$ and $\{v_2(\mathbf{r}),\mathcal{X}_2\}$ are trivially different, so that their ground-state wave functions are interchangeable. Equation (A6) indicates that if one chooses $\{v(\mathbf{r}),\mathcal{X}\}$ incorrectly, then the value of $F_{\rho,\mathbf{X}}$ will be too small, and that the maximum value for $F_{\rho,\mathbf{X}}$, if it exists, occurs for the external potential $v(\mathbf{r})$ and the property potential $\mathcal{X}$, for which $\{\rho(\mathbf{r}),\mathbf{X}\}$ is the ground state. It then follows from the definition of $F_{\rho,\mathbf{X}}$ that the ground-state energy is exact, e.g., from Eq. (A6),

$$F_{\rho_2,\mathbf{X}_2}[v_2,\mathcal{X}_2,N]+\int\rho_2(\mathbf{r})v_2(\mathbf{r})d\mathbf{r}+\langle\mathcal{X}_2,\mathbf{X}_2\rangle=E_{gs}[v_2,\mathcal{X}_2,N].\tag{A7}$$

(3) The variational principle holds, even when $\{\rho(\mathbf{r}),\mathbf{X}\}$ is not N representable. Given *any* electron density $\rho(\mathbf{r})$ and a property value $\mathbf{X}$, then for every $\{v_0(\mathbf{r}),\mathcal{X}_0\}$,

$$F[\rho,\mathbf{X}]+\int\rho(\mathbf{r})v_0(\mathbf{r})d\mathbf{r}+\langle\mathcal{X}_0,\mathbf{X}\rangle\ge E_{gs}[v_0,\mathcal{X}_0,N].\tag{A8}$$

That the equality only holds if $\{\rho(\mathbf{r}),\mathbf{X}\}$ is the ground state for $\{v_0(\mathbf{r}),\mathcal{X}_0\}$ was established in the previous paragraph. Notice that the variational relation in Eq. (A8) holds for every possible $\{\rho(\mathbf{r}),\mathbf{X}\}$, whether it is N-representable or not. The variational relation even holds for *absurd* choices; one can, for example, choose an electron density that is negative in some regions. If the property of interest is the exchange energy, a positive exchange energy can be chosen, even though this is physically absurd. The functional is still defined.

(4) The functionals are convex, so the minimum is unique. This result follows from the definition of the functional and the fact that the maximum (or supremum) of a sum is greater than the sum of the maxima (or suprema). Specifically,

$$\begin{aligned}&F[t\rho_1+(1-t)\rho_2,t\mathbf{X}_1+(1-t)\mathbf{X}_2]\\ &\quad=\underbrace{\sup}_{v(\mathbf{r}),\mathcal{X}}\Bigg\{t\Bigg(E_{gs}[v,\mathcal{X},N]-\int\rho_1(\mathbf{r})v(\mathbf{r})d\mathbf{r}-\langle\mathcal{X},\mathbf{X}_1\rangle\Bigg)\\ &\qquad+(1-t)\Bigg(E_{gs}[v,\mathcal{X},N]-\int\rho_2(\mathbf{r})v(\mathbf{r})d\mathbf{r}-\langle\mathcal{X},\mathbf{X}_2\rangle\Bigg)\Bigg\}\\ &\quad\le t\underbrace{\sup}_{v(\mathbf{r}),\mathcal{X}}\Bigg(E_{gs}[v,\mathcal{X},N]-\int\rho_1(\mathbf{r})v(\mathbf{r})d\mathbf{r}-\langle\mathcal{X},\mathbf{X}_1\rangle\Bigg)\\ &\qquad+(1-t)\underbrace{\sup}_{v(\mathbf{r}),\mathcal{X}}\Bigg(E_{gs}[v,\mathcal{X},N]-\int\rho_2(\mathbf{r})v(\mathbf{r})d\mathbf{r}-\langle\mathcal{X},\mathbf{X}_2\rangle\Bigg)\\ &\quad=tF[\rho_1,\mathbf{X}_1]+(1-t)F[\rho_2,\mathbf{X}_2].\end{aligned}\tag{A9}$$

(5) The unrestricted functionals are infinity for non-N-representable cases. Suppose that $\{\tilde{\rho}(\mathbf{r}),\tilde{\mathbf{X}}\}$ are not ensemble-N-representable. That is, there is no N-electron density matrix that has electron density $\tilde{\rho}(\mathbf{r})$ and property value $\tilde{\mathbf{X}}$. It follows from the expression for the N-electron density matrix in terms of pure states

$$\Gamma_N=\sum_{i=1}^{\infty}w_i|\Psi_i\rangle\langle\Psi_i|,$$

$$0\le w_i\le1,\quad 1=\sum_{i=1}^{\infty}w_i\tag{A10}$$

that the set of ensemble-N-representable $\{\rho(\mathbf{r}),\mathbf{X}\}$ is closed and convex. This means that the distance between $\{\tilde{\rho}(\mathbf{r}),\tilde{\mathbf{X}}\}$ and the set of ensemble-N-representable $\{\rho(\mathbf{r}),\mathbf{X}\}$ is some positive number $\tilde{d}$.

A lower bound to $F[\tilde{\rho},\tilde{\mathbf{X}}]$ can be constructed by considering any guess that arises as an intermediate step in the supremization procedure

$$\begin{aligned}F[\tilde{\rho},\tilde{\mathbf{X}}]&\ge F_{\tilde{\rho},\tilde{\mathbf{X}}}[v_0,\mathcal{X}_0,N]\\ &=E_{gs}[v_0,\mathcal{X}_0,N]-\int\tilde{\rho}(\mathbf{r})v_0(\mathbf{r})d\mathbf{r}-\langle\mathcal{X}_0,\tilde{\mathbf{X}}\rangle.\end{aligned}\tag{A11}$$

We will try to find a way to change $\{v_0(\mathbf{r}),\mathcal{X}_0\}$ to form a tighter lower bound. From the dual relationship between $\rho(\mathbf{r})$

and $v(\mathbf{r})$, and between $\mathbf{X}$ and $\mathcal{X}$, we have that

$$\frac{\delta E_{gs}[v_0,\mathcal{X}_0,N]}{\delta v(\mathbf{r})} = \rho_0(\mathbf{r}),$$

$$\frac{\delta E_{gs}[v_0,\mathcal{X}_0,N]}{\delta \mathcal{X}(\mathbf{r})} = \mathbf{X}_0, \tag{A12}$$

where $\rho_0(\mathbf{r})$ and $\mathbf{X}_0$ are the ground-state density and the property value from the variational principle for the energy in Eq. (14). $\{\rho_0(\mathbf{r}),\mathbf{X}_0\}$ is obviously N-representable so the distance between $\{\rho_0(\mathbf{r}),\mathbf{X}_0\}$ and $\{\tilde{\rho}(\mathbf{r}),\tilde{\mathbf{X}}\}$ is at least $\tilde{d}$. From Eq. (A12) and the definition of the functional derivative,

$$E_{gs}[v_1,\mathcal{X}_1,N] - E_{gs}[v_0,\mathcal{X}_0,N] \approx \int \rho_0(\mathbf{r})[v_1(\mathbf{r}) - v_0(\mathbf{r})]d\mathbf{r} + \langle \mathcal{X}_1 - \mathcal{X}_0, \mathbf{X}_0\rangle, \tag{A13}$$

and so

$$F_{\tilde{\rho},\tilde{\mathbf{X}}}[v_1,\mathcal{X}_1,N] - F_{\tilde{\rho},\tilde{\mathbf{X}}}[v_0,\mathcal{X}_0,N] \approx \int [\rho_0(\mathbf{r}) - \tilde{\rho}(\mathbf{r})][v_1(\mathbf{r}) - v_0(\mathbf{r})]d\mathbf{r} + \langle \mathcal{X}_1 - \mathcal{X}_0, \mathbf{X}_0 - \tilde{\mathbf{X}}\rangle. \tag{A14}$$

Because the distance between $\{\rho_0(\mathbf{r}),\mathbf{X}_0\}$ and $\{\tilde{\rho}(\mathbf{r}),\tilde{\mathbf{X}}\}$ is at least $\tilde{d}$, there exists a linear operator

$$\{\delta v(\mathbf{r}), \delta\mathcal{X}\} \tag{A15}$$

with norm 1 for which

$$\tilde{d} \le \int [\rho_0(\mathbf{r}) - \tilde{\rho}(\mathbf{r})]\delta v(\mathbf{r})d\mathbf{r} + \langle \delta\mathcal{X}, \mathbf{X}_0 - \tilde{\mathbf{X}}\rangle. \tag{A16}$$

Find one such linear operator and define $v_1(\mathbf{r}) = v_0(\mathbf{r}) + \varepsilon(\delta v(\mathbf{r}))$ and $\mathcal{X}_1 = \mathcal{X}_0 + \varepsilon(\delta\mathcal{X})$. Choose the value of ε, so that $F_{\tilde{\rho},\tilde{\mathbf{X}}}[v_1,\mathcal{X}_1,N]$ is as large as possible. [Note that ε may be less than 1, because the perturbation formula (A13) is not valid for large perturbations.]

The ground-state density and the property value for $\{v_1(\mathbf{r}),\mathcal{X}_1\}$ is also at least $\tilde{d}$ units from $\{\tilde{\rho}(\mathbf{r}),\tilde{\mathbf{X}}\}$, so we can repeat the procedure and construct a new lower bound $F_{\tilde{\rho},\tilde{\mathbf{X}}}[v_2,\mathcal{X}_2,N]$ that is appreciably bigger than $F_{\tilde{\rho},\tilde{\mathbf{X}}}[v_1,\mathcal{X}_1,N]$. Continuing this procedure *ad infinitum* allows one to produce a sequence of lower bounds,

$$F[\tilde{\rho},\tilde{\mathbf{X}}] > F_{\tilde{\rho},\tilde{\mathbf{X}}}[v_k,\mathcal{X}_k,N]. \tag{A17}$$

However, the preceding argument means that we can construct a sequence of lower bounds that diverges: $F_{\tilde{\rho},\tilde{\mathbf{X}}}[v_k,\mathcal{X}_k,N] \to \infty$ as $k \to \infty$. So it must be that $F[\tilde{\rho},\tilde{\mathbf{X}}] = \infty$ for non-ensemble-N-representable $\{\tilde{\rho}(\mathbf{r}),\tilde{\mathbf{X}}\}$. This result is a generalization of several special cases that are known in the literature [11,52].

(6) If both functionals are defined, then the partial Legendre transform functional is an upper bound to the full Legendre transform functional. We will show that $F[\rho,\mathbf{X}]$ is the smallest possible functional that is consistent with the variational principle. It then follows that any other functional that is also exact must be greater than or equal to this functional. Ergo, $F_{\mathbf{X}}[\rho] \ge F[\rho,\mathbf{X}]$.

Suppose that there is a functional $F^{<}[\rho,\mathbf{X}]$ that is less than $F[\rho,\mathbf{X}]$ for some $\{\rho_0(\mathbf{r}),\mathbf{X}_0\}$. Then there exists some $\varepsilon > 0$ such that $F[\rho_0,\mathbf{X}_0] - F^{<}[\rho_0,\mathbf{X}_0] > \varepsilon$. Since

$$\underbrace{\sup}_{v(\mathbf{r}),\mathcal{X}} \left\{E_{gs}[v;\mathcal{X},N] - \int \rho_0(\mathbf{r})v(\mathbf{r})d\mathbf{r} - \langle\mathcal{X},\mathbf{X}_0\rangle\right\} - F^{<}[\rho_0,\mathbf{X}_0] > \varepsilon, \tag{A18}$$

there must exist some external potential and property potential such that

$$E_{gs}[\tilde{v};\tilde{\mathcal{X}},N] - \int \rho_0(\mathbf{r})\tilde{v}(\mathbf{r})d\mathbf{r} - \langle\tilde{\mathcal{X}},\mathbf{X}_0\rangle - F^{<}[\rho_0,\mathbf{X}_0] > \varepsilon, \tag{A19}$$

and so

$$\begin{aligned} E_{gs}[\tilde{v};\tilde{\mathcal{X}},N] &> \varepsilon + F^{<}[\rho_0,\mathbf{X}_0] + \int \rho_0(\mathbf{r})\tilde{v}(\mathbf{r})d\mathbf{r} + \langle\tilde{\mathcal{X}},\mathbf{X}_0\rangle \\ &> F^{<}[\rho_0,\mathbf{X}_0] + \int \rho_0(\mathbf{r})\tilde{v}(\mathbf{r})d\mathbf{r} + \langle\tilde{\mathcal{X}},\mathbf{X}_0\rangle. \end{aligned} \tag{A20}$$

That is, there is some system for which the variational principle is invalid. Notice that this need not be a physically relevant system. The restricted Legendre transform functionals are a special case where $F^{<}[\rho,\mathbf{X}]$ is guaranteed to be exact and variational for the systems that the user finds "physically relevant," even though the functional may fail (and fail infinitely badly) for other systems.

(7) If both functionals are defined, then the extended constrained-search functional is an upper bound to the partial Legendre transform functional. This result could be proved using an argument very similar to the one in the previous paragraph, but it is perhaps more interesting to provide a totally different derivation, based on the result in Ref. [9]. The extended constrained-search functional is

$$F_{\mathbf{X}}^{\mathrm{xCS}}[\rho] = \underbrace{\min}_{\Psi\to\{\rho(\mathbf{r}),\mathbf{X}\}} \langle\Psi|\hat{F}|\Psi\rangle, \tag{A21}$$

where $\hat{F} = \hat{T} + V_{ee}$. Add and subtract $\int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r}$ to obtain

$$F_{\mathbf{X}}^{\mathrm{xCS}}[\rho] = \left(\underbrace{\min}_{\Psi\to\{\rho(\mathbf{r}),\mathbf{X}\}} \langle\Psi|\hat{F} + \sum_{i=1}^{N} v(\mathbf{r}_i)|\Psi\rangle\right) - \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r}. \tag{A22}$$

Now, relax the constraint that the wave function must have the density $\rho(\mathbf{r})$. Relaxing the constraint gives the inequality

$$F_{\mathbf{X}}^{\text{xCS}}[\rho] \geq \left(\underbrace{\min}_{\Psi\to\mathbf{X}} \langle \Psi | \hat{F} + \sum_{i=1}^{N} v(\mathbf{r}_i) | \Psi \rangle \right) - \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r}$$
$$= E_{gs}[v,\mathbf{X};N] - \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r}. \tag{A23}$$

This inequality is true for *any* external potential, so one can take the supremum of the right-hand side as

$$F_{\mathbf{X}}^{\text{xCS}}[\rho] \geq \underbrace{\sup}_{v} \left\{ E_{gs}[v,\mathbf{X};N] - \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \right\} = F_{\mathbf{X}}[\rho]. \tag{A24}$$

The equality is true only if there exists some external potential for which the equality in Eq. (A23) holds, so that

$$F_{\mathbf{X}}^{\text{xCS}}[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} = E_{gs}[v,\mathbf{X};N]. \tag{A25}$$

That is, the equality is true only if, among systems with property $\mathbf{X}$, $\rho(\mathbf{r})$ is pure-state v-representable.

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[2] H. Englisch and R. Englisch, Phys. Status Solidi B **123**, 711 (1984).
[3] H. Englisch and R. Englisch, Phys. Status Solidi B **124**, 373 (1984).
[4] H. Englisch and R. Englisch, Physica A **121**, 253 (1983).
[5] P. W. Ayers, Phys. Rev. A **73**, 012513 (2006).
[6] T. Heaton-Burgess, P. Ayers, and W. T. Yang, Phys. Rev. Lett. **98**, 036403 (2007).
[7] W. T. Yang, P. W. Ayers, and Q. Wu, Phys. Rev. Lett. **92**, 146404 (2004).
[8] M. Levy, Proc. Natl. Acad. Sci. U.S.A. **76**, 6062 (1979).
[9] M. Levy and J. P. Perdew, NATO ASI Ser., Ser. B **123**, 11 (1985).
[10] S. M. Valone, J. Chem. Phys. **73**, 4653 (1980).
[11] E. H. Lieb, Int. J. Quantum Chem. **24**, 243 (1983).
[12] W. Kutzelnigg, J. Mol. Struct.: THEOCHEM **768**, 163 (2006).
[13] T. L. Gilbert, Phys. Rev. B **12**, 2111 (1975).
[14] J. E. Harriman, Phys. Rev. A **24**, 680 (1981).
[15] P. W. Ayers, Theor. Chem. Acc. **110**, 267 (2003).
[16] P. W. Ayers and A. Nagy, J. Chem. Phys. **126**, 144108 (2007).
[17] P. W. Ayers, Chem. Phys. Lett. **438**, 148 (2007).
[18] P. W. Ayers, Proc. Natl. Acad. Sci. U.S.A. **97**, 1959 (2000).
[19] P. W. Ayers, Phys. Rev. A **71**, 062506 (2005).
[20] P. W. Ayers, F. De Proft, and P. Geerlings, Phys. Rev. A **75**, 012508 (2007).
[21] F. De Proft *et al.*, J. Chem. Phys. **120**, 9969 (2004).
[22] A. K. Rajagopal and J. Callaway, Phys. Rev. B **7**, 1912 (1973).
[23] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).
[24] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[25] G. Vignale and M. Rasolt, Phys. Rev. Lett. **59**, 2360 (1987).
[26] G. Vignale and M. Rasolt, Phys. Rev. B **37**, 10685 (1988).
[27] R. A. Donnelly and R. G. Parr, J. Chem. Phys. **69**, 4431 (1978).
[28] P. O. Lowdin, Phys. Rev. **97**, 1474 (1955).
[29] J. Coleman, Rev. Mod. Phys. **35**, 668 (1963).
[30] E. R. Davidson, *Reduced Density Matrices in Quantum Chemistry* (Academic Press, New York, 1976).
[31] C. Garrod and J. K. Percus, J. Math. Phys. **5**, 1756 (1964).
[32] D. A. Mazziotti, Acc. Chem. Res. **39**, 207 (2006).
[33] P. Ziesche, Phys. Lett. A **195**, 213 (1994).
[34] P. Ziesche, Int. J. Quantum Chem. **60**, 1361 (1996).
[35] A. Gonis, T. C. Schulthess, J. van Ek, and P. E. A. Turchi, Phys. Rev. Lett. **77**, 2981 (1996).
[36] A. Gonis, T. C. Schulthess, P. E. A. Turchi, and J. van Ek, Phys. Rev. B **56**, 9335 (1997).
[37] P. W. Ayers, J. Math. Phys. **46**, 062107 (2005).
[38] P. W. Ayers, Phys. Rev. A **74**, 042502 (2006).
[39] A. Nagy and C. Amovilli, J. Chem. Phys. **121**, 6640 (2004).
[40] A. Nagy, Phys. Rev. A **66**, 022505 (2002).
[41] M. Higuchi and K. Higuchi, Physica B **387**, 117 (2007).
[42] M. Higuchi *et al.*, J. Magn. Magn. Mater. **310**, 990 (2007).
[43] F. Furche, Phys. Rev. A **70**, 022514 (2004).
[44] B. Liu and J. K. Percus, Phys. Rev. A **74**, 012508 (2006).
[45] J. K. Percus, J. Chem. Phys. **122**, 234103 (2005).
[46] P. Gori-Giorgi and A. Savin, Philos. Mag. **86**, 2643 (2006).
[47] A. Nagy, J. Chem. Phys. **125**, 184104 (2006).
[48] P. Gori-Giorgi and A. Savin, Phys. Rev. A **71**, 032513 (2005).
[49] P. Gori-Giorgi and A. Savin, J. Chem. Theory Comput. **3**, 796 (2007).
[50] D. Van Neck, S. Verdonck, G. Bonny, P. W. Ayers, and M. Waroquier, Phys. Rev. A **74**, 042501 (2006).
[51] S. Verdonck, D. Van Neck, P. W. Ayers, and M. Waroquier, Phys. Rev. A **74**, 062503 (2006).
[52] P. W. Ayers, S. Golden, and M. Levy, J. Chem. Phys. **124**, 054101 (2006).
[53] P. W. Ayers and M. Levy, J. Chem. Sci. **117**, 507 (2005).
[54] K. Higuchi and M. Higuchi, Phys. Rev. B **69**, 165118 (2004).
[55] K. Higuchi and M. Higuchi, J. Magn. Magn. Mater. **272-276**, 659 (2004).
[56] M. Higuchi and K. Higuchi, Phys. Rev. B **69**, 035113 (2004).
[57] K. Higuchi and M. Higuchi, Phys. Rev. A **79**, 022113 (2009).
[58] K. Higuchi and M. Higuchi, Phys. Rev. B **71**, 035116 (2005).
[59] H. Eschrig and W. E. Pickett, Solid State Commun. **118**, 123 (2001).
[60] K. Capelle and V. L. Libero, Int. J. Quantum Chem. **105**, 679 (2005).
[61] K. Capelle and G. Vignale, Phys. Rev. B **65**, 113106 (2002).
[62] K. Capelle and G. Vignale, Phys. Rev. Lett. **86**, 5546 (2001).
[63] N. Argaman and G. Makov, Phys. Rev. B **66**, 052413 (2002).
[64] C. A. Ullrich, Phys. Rev. B **72**, 073102 (2005).
[65] W. Kohn, A. Savin, and C. A. Ullrich, Int. J. Quantum Chem. **100**, 20 (2004).
[66] S. Pittalis, S. Kurth, N. Helbig, and E. K. U. Gross, Phys. Rev. A **74**, 062511 (2006).
[67] S. Baroni and E. Tuncel, J. Chem. Phys. **79**, 6140 (1983).
[68] A. Gorling and M. Levy, J. Chem. Phys. **106**, 2675 (1997).

[69] S. Ivanov and M. Levy, Theor. Chem. Acc. **103**, 117 (1999).
[70] P. W. Ayers and S. B. Liu, Phys. Rev. A **75**, 022514 (2007).
[71] E. V. Ludena, J. Mol. Struct.: THEOCHEM **709**, 25 (2004).
[72] E. S. Kryachko and E. V. Ludena, Phys. Rev. A **43**, 2179 (1991).
[73] P. Mori-Sanchez, A. J. Cohen, and W. T. Yang, J. Chem. Phys. **125**, 201102 (2006).
[74] M. M. Odashima and K. Capelle, J. Chem. Phys. **127**, 054106 (2007).
[75] Garnet Kin-Lic Chan and N. C. Handy, Phys. Rev. A **59**, 3075 (1999).
[76] E. H. Lieb and S. Oxford, Int. J. Quantum Chem. **19**, 427 (1981).
[77] M. M. Odashima and K. Capelle, Int. J. Quantum Chem. **108**, 2428 (2008).
[78] M. Higuchi and K. Higuchi, Phys. Rev. B **78**, 125101 (2008).
[79] K. Higuchi and M. Higuchi, J. Phys.: Condens. Matter **21**, 064206 (2009).
[80] P. W. Ayers and E. R. Davidson, Int. J. Quantum Chem. **106**, 1487 (2006).
[81] E. R. Davidson, Chem. Phys. Lett. **246**, 209 (1995).
[82] M. E. Pistol, Chem. Phys. Lett. **417**, 521 (2006).
[83] M. E. Pistol, Chem. Phys. Lett. **422**, 363 (2006).
[84] M. E. Pistol, Chem. Phys. Lett. **400**, 548 (2004).
[85] M. Higuchi *et al.*, J. Phys.: Condens. Matter **19**, 365219 (2007).
[86] M. Higuchi and K. Higuchi, Phys. Rev. A **75**, 042510 (2007).
[87] Denote the set of pairings between $\mathbf{X}$ and $\rho(\mathbf{r})$ that can be attained from Slater determinant wave functions as $S_{\mathrm{X},\rho}$. For most choices of $\mathbf{X}$, the number of elements in $S_{\mathrm{X},\rho}$ is infinitely smaller than the number of elements in the complement of $S_{\mathrm{X},\rho}$.
[88] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. **49**, 1691 (1982).
[89] W. T. Yang, Y. K. Zhang, and P. W. Ayers, Phys. Rev. Lett. **84**, 5172 (2000).
[90] P. W. Ayers, J. Math. Chem. **43**, 285 (2008).
[91] P. Gori-Giorgi and A. Savin, Int. J. Mod. Phys. B **21**, 2449 (2007).
[92] P. W. Ayers and W. T. Yang, J. Chem. Phys. **124**, 224108 (2006).
[93] A. Holas and R. Balawender, J. Chem. Phys. **125**, 247101 (2006).
[94] R. F. Nalewajski and R. G. Parr, J. Chem. Phys. **77**, 399 (1982).
[95] Y. K. Zhang and W. T. Yang, Theor. Chem. Acc. **103**, 346 (2000).
[96] S. Keinan *et al.*, J. Phys. Chem. A **111**, 176 (2007).
[97] M. L. Wang *et al.*, J. Am. Chem. Soc. **128**, 3228 (2006).
[98] O. A. von Lilienfeld and M. E. Tuckerman, J. Chem. Phys. **125**, 154104 (2006).
[99] O. A. von Lilienfeld, R. D. Lins, and U. Rothlisberger, Phys. Rev. Lett. **95**, 153002 (2005).
[100] P. W. Ayers and R. G. Parr, J. Am. Chem. Soc. **123**, 2007 (2001).
[101] A. Cedillo *et al.*, J. Phys. Chem. A **111**, 2442 (2007).
[102] J. Harris and R. O. Jones, J. Phys. F: Met. Phys. **4**, 1170 (1974).
[103] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).
[104] D. C. Langreth and J. P. Perdew, Phys. Rev. B **15**, 2884 (1977).
[105] M. Levy and J. P. Perdew, Phys. Rev. A **32**, 2010 (1985).
[106] W. Yang, J. Chem. Phys. **109**, 10107 (1998).