

Hartree and Exchange in Ensemble Density Functional Theory: Avoiding the Nonuniqueness Disaster

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Ensemble density functional theory is a promising method for the efficient and accurate calculation of excitations of quantum systems, at least if useful functionals can be developed to broaden its domain of practical applicability. Here, we introduce a guaranteed single-valued “Hartree-exchange” ensemble density functional, $\mathcal{E}_{\text{HX}}[n]$, in terms of the right derivative of the universal ensemble density functional with respect to the coupling constant at vanishing interaction. We show that $\mathcal{E}_{\text{HX}}[n]$ is straightforwardly expressible using block eigenvalues of a simple matrix [Eq. (14)]. Specialized expressions for $\mathcal{E}_{\text{HX}}[n]$ from the literature, including those involving superpositions of Slater determinants, can now be regarded as originating from the unifying picture presented here. We thus establish a clear and practical description for Hartree and exchange in ensemble systems.

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Density functional theory [1,2] (DFT) is, arguably, the most important methodology in electronic structure theory due to its remarkable accuracy in numerically efficient approximations. But “open” systems that mix different numbers of electrons, degenerate ground states, and excited states have long posed a challenge to conventional approaches (see, e.g., Refs. [3–9]), and can make even qualitative accuracy very difficult to achieve. One promising route around these problems is to employ ensemble density functional theory [10–17] (EDFT), in which ensembles of quantum states extend the original pure state approach of DFT to such systems. As many quantum systems [18,19] are better understood by models involving ensembles, ideas and constructions at the heart of EDFT offer a more promising approach for their study, compared to conventional DFT. The ability to use EDFT as successfully and easily as we now use DFT could thus transform quantitative understanding of numerous quantum systems and processes, such as charge transfer and diabatic reactions.

In standard DFT, we decompose the universal functional, F , of the particle density n , as

$$F[n] = T_s[n] + E_{\text{HX}}[n] + E_c[n], \quad (1)$$

where T_s is the kinetic-energy density of the Kohn-Sham (KS) reference system,

$$E_{\text{HX}}[n] = \int \frac{d\mathbf{r}d\mathbf{r}'}{2|\mathbf{r}-\mathbf{r}'|} \{n(\mathbf{r})n(\mathbf{r}') - |\rho_s(\mathbf{r},\mathbf{r}')|^2\}, \quad (2)$$

is the Hartree energy plus the exchange energy—in which $\rho_s(\mathbf{r},\mathbf{r}')$ is the KS one-body reduced density matrix and $n(\mathbf{r}) = \rho_s(\mathbf{r},\mathbf{r})$ equals the interacting ground state particle density—and $E_c[n]$ is the correlation energy.

It may be tempting to switch to EDFT by replacing the pure state quantities with ensembles (statistical mixtures of pure states) by performing a simple replacement of the particle density by its ensemble generalization. We thus set $\rho_s(\mathbf{r},\mathbf{r}') \rightarrow \text{Tr}[\hat{\Gamma}_0^n \hat{\rho}(\mathbf{r},\mathbf{r}')]$ where $\hat{\Gamma}_0^n$ is the “ensemble density matrix” operator describing the reference Kohn-Sham state, and use $\text{Tr}[\hat{\Gamma}_0^n \hat{\rho}(\mathbf{r},\mathbf{r})] = n(\mathbf{r})$ to write

$$E_{\text{HX}}[n] \rightarrow \int \frac{d\mathbf{r}d\mathbf{r}'}{2|\mathbf{r}-\mathbf{r}'|} \{n(\mathbf{r})n(\mathbf{r}') - |\text{Tr}[\hat{\Gamma}_0^n \hat{\rho}(\mathbf{r},\mathbf{r}')]|^2\}.$$

This, however, comes at the price of introducing spurious “ghost interactions” to both the Hartree and exchange terms—with sometimes disastrous consequences in approximate calculation [20].

A ghost interaction error can be understood as a generalization of the one- or N -particle self-interaction error [4]. But, rather than an orbital spuriously interacting with itself it instead spuriously interacts with its ghost counterpart in a different replica of the same system. From this understanding comes a desire to correct these ghost interactions in the Hartree and exchange energies. A formal justification of these corrections was put forward by Gidopoulos *et al.* [20] by importing the result for the Hartree-Fock approximations for ensembles—which was noticed to be ghost-interaction free for the cases considered in the same cited work—and then invoking an extended optimized effective potential method [21–23], as in pure state exchange theory.

The principle espoused by Gidopoulos *et al.* is clear. Unpleasantly, however, the resulting prescription must be worked out for each case at hand. This process entails rather tedious and system-specific bookkeeping. For

specific cases, the expression of the resulting functional may be found in the original literature [5,20,24,25].

Matters are simplified somewhat by working with combined Hartree-exchange (Hx) expressions to avoid difficulties of treating the components individually as in $\text{Tr}[\hat{\Gamma}_s \hat{W}]$ where \hat{W} is the electron-electron interacting operator. This approach has been elaborated further in Nagy's works [23,26] showing how ghost-interaction-free Hartree plus exchange-correlation functionals can be defined in terms of a weighted sum of energies of the states in the ensembles. Such an approach resolves many problems and is, indeed, correct in many instances. Very recently, the evolution of Hartree and exchange in EDFT has culminated with the proposal of a symmetrized eigenstate Hartree-exchange expression [27–29].

In this work, we put forward a universal and unifying treatment of Hartree and exchange in EDFT that encompasses other specialized Hartree-exchange expressions—when appropriate. We start from the observation that using $\text{Tr}[\hat{\Gamma} \hat{W}]$ too directly can lead to subtle fundamental issues. As we illustrate, this occurs in the presence of particular forms of degeneracies in the many-body quantum states for which $\text{Tr}[\hat{\Gamma} \hat{W}]$ is not characterized by a unique value, as happens when the same ensemble particle density may be obtained from different $\hat{\Gamma}$. In such cases the possibility of extracting a simple single-valued expression for a corresponding Hartree-exchange ensemble density functional is far from obvious. The goal of this work is to avoid such a “nonuniqueness disaster,” and thus develop a functional that can be used directly or approximated for calculations.

We show that a general approach free from pathologies follows directly from a definition of Hartree and exchange that avoids a direct reference to the Hartree-Fock method by working consistently within EDFT. The core of the idea is to exploit the “nice” properties of the exact universal interacting functionals, $\mathcal{F}^\lambda[n]$ [see Eq. (5) and prior discussion], and its Kohn-Sham version, the kinetic energy density functional $\mathcal{T}_s[n] \equiv \mathcal{F}^0[n]$, by defining

$$\mathcal{E}_{\text{Hx}}[n] := \lim_{\lambda \rightarrow 0^+} \frac{\mathcal{F}^\lambda[n] - \mathcal{T}_s[n]}{\lambda}, \quad (3)$$

where λ stands for the continuously varying strength of the electron-electron interaction coupling operator \hat{W} . Obviously, the companion correlation functional for $\mathcal{E}_{\text{Hx}}[n]$ must be $\mathcal{E}_c[n] := \mathcal{F}^1[n] - \mathcal{T}_s[n] - \mathcal{E}_{\text{Hx}}[n]$.

As we illustrate, Eq. (3) has several convenient corollaries [Eqs. (10), (13), and (14)]. For now, we highlight that it can be restated in terms of a minimization

$$\mathcal{E}_{\text{Hx}}[n] \equiv \min_{\hat{\Gamma} \in \mathcal{G}^{n,\lambda=0}} \text{Tr}[\hat{\Gamma} \hat{W}], \quad (4)$$

where $\mathcal{G}^{n,\lambda=0}$ is the set of the noninteracting ensembles that yield the prescribed particle density n and the exact Kohn-Sham kinetic energy $\mathcal{T}_s[n]$. Crucially, here the conventional

restriction to single Slater determinant must be avoided, and we must concern ourselves only with the uniqueness of $\mathcal{E}_{\text{Hx}}[n]$ and not the states $\hat{\Gamma}$ that yield it.

From (3) and (4) we can gain several important insights of both formal and practical use (in the remainder of the paper, we come back on the following points by providing further details or explicit examples).

Avoidance of the nonuniqueness disaster: $\text{Tr}[\hat{\Gamma} \hat{W}]$ can assume different values on different states $\hat{\Gamma}$ having equal kinetic energy and equal densities. In this situation, a functional expression directly based on $\text{Tr}[\hat{\Gamma} \hat{W}]$ does not provide a unique value for a given density. $\mathcal{E}_{\text{Hx}}[n]$, instead, picks automatically the minimum value. In other words, $\mathcal{E}_{\text{Hx}}[n]$ is guaranteed to acquire unique values for each given n , regardless of any nonuniqueness of $\hat{\Gamma} \rightarrow n$.

Maximal freedom from interactions: It is reassuring to note that avoiding the nonuniqueness disaster does not play against avoiding the spurious interactions we discussed above. This readily follows from the fact that $\mathcal{E}_{\text{Hx}}[n]$ is determined by a minimization of the expectation value of the interaction energy. Therefore, it must also be maximally free from spurious interactions—as much as the constraints underlying the construction of $\mathcal{G}^{n,\lambda=0}$ can allow.

Multireference states: It also becomes apparent that all the nice properties of $\mathcal{E}_{\text{Hx}}[n]$ induced by $\mathcal{F}^\lambda[n]$ can be spoiled by restrictions on the underlying admissible ensembles. In some situations, described later, insistence on using single Slater determinants, as in conventional Kohn-Sham theory, is overly restrictive in EDFT.

In the remainder of this paper we first explore the derivation of, and consequences of, this unifying picture of Hartree-exchange physics. Finally we conclude.

Let us first consider some background theory, and define some key concepts. Ensemble DFT [10–12,14] overcomes the restriction of standard Kohn-Sham theory to pure states. Thus, it can be used to widely generalize the systems that can be studied using DFT. First, we can form ensembles $\hat{\Gamma} = \sum_{\kappa} w_{\kappa} |\kappa\rangle \langle \kappa|$ that mix degenerate states, such that $\text{Tr}[\hat{H} \hat{\Gamma}^{\text{degen}}] = \sum_{\kappa} w_{\kappa} E_0 = E_0$ for the appropriate Hamiltonian \hat{H} . Secondly, we can form ensembles that involve excited states, provided the weights do not increase as the energy increases. Thus, $\text{Tr}[\hat{H} \hat{\Gamma}^{\text{excite}}] = \sum_{\kappa} w_{\kappa} E_{\kappa} \geq E_0$, and the energy can be higher than the equivalent ground state $E_0 = \langle 0 | \hat{H} | 0 \rangle$. The degenerate case above is, in fact, an important specialized version of this type of ensemble. For the sake of simplicity, we do not consider ensembles that mix different numbers of electrons (open states).

In order to account for the aforementioned cases, some constraints, which we indicate collectively as \mathcal{C} , must be enforced to suit the problem, e.g., to select certain fractions of ground and excited states or to preserve certain symmetries on the system. Moreover, since Eq. (3) invokes the use of the adiabatic coupling, they must define weights at

varying electron interaction strength λ that reproduce the particle density at full interaction, a nontrivial task. The present work relies on two primary, physically reasonable restrictions on the allowed ensembles: (i) they must describe a finite number of “typical” states with weights that can change only at an energy-level crossing so that $\exists \delta > 0$ where $w_\kappa^\lambda = w_\kappa^0, \forall 0 \leq \lambda < \delta$; (ii) the density n must be ensemble v representable for $0 \leq \lambda < \delta$ so that we can invoke the theorems of Gross-Oliveira-Kohn [15–17] to define $\mathcal{F}^\lambda[n]$.

In the parlance of the constrained search approach, one can then define a general universal functional

$$\mathcal{F}_C^\lambda[n] = \min_{\hat{\Gamma}_C} \text{Tr}[\hat{\Gamma}(\hat{T} + \lambda\hat{W})], \quad (5)$$

where the minimization (strictly an infimum) is carried out over density matrices $\hat{\Gamma}_C$ constrained to give a density $n = \text{Tr}[\hat{\Gamma}_C \hat{n}]$ by means of orthonormal states and a prescribed set of weights w_κ^λ . \hat{T} is a kinetic energy operator and \hat{W} is a positive-definite two-point interaction operator. For what follows, however, we only need to be concerned with $0 \leq \lambda < \delta$ and $\lambda = 1$.

The universal functional (5) then allows us to find the energy and density of any Hamiltonian $\{\hat{T} + \hat{W} + \hat{v}_{\text{Ext}}\}$ by seeking

$$\mathcal{E}[v_{\text{Ext}}] = \min_{n \rightarrow N} \left(\mathcal{F}[n] + \int d\mathbf{r} n(\mathbf{r}) v_{\text{Ext}}(\mathbf{r}) \right), \quad (6)$$

where $\mathcal{F}[n] = \mathcal{F}^1[n] = \mathcal{T}_s[n] + \mathcal{E}_{\text{Hxc}}[n]$ and $v_{\text{Ext}}(\mathbf{r})$ is an external (local) multiplicative potential. We use \mathcal{F}^λ to define the Kohn-Sham kinetic energy $\mathcal{T}_s[n] = \mathcal{F}^0[n]$ and Hartree, exchange, and correlation (Hxc) energy $\mathcal{E}_{\text{Hxc}}[n] = \mathcal{F}[n] - \mathcal{T}_s[n]$ at given density n . Here and henceforth \mathcal{C} is left off for succinctness, unless strictly necessary to improve clarity.

Now, let us analyze the Hx energy definition

$$\mathcal{E}_{\text{Hx}}[n] := \lim_{\lambda \rightarrow 0^+} \frac{\mathcal{F}^\lambda[n] - \mathcal{F}^0[n]}{\lambda} \equiv \partial_\lambda \mathcal{F}^\lambda[n]|_{\lambda=0^+}. \quad (7)$$

First, let us assume that there is a unique interacting ensemble $\hat{\Gamma}^{n,\lambda}$, which is connected perturbatively to a noninteracting one $\hat{\Gamma}^{n,0}$ along the adiabatic connection. Consider the case for which nondegenerate perturbation theory applies (the degenerate case is considered below). For $\lambda \ll 1$, we can write

$$\hat{\Gamma}^{n,\lambda} \approx \hat{\Gamma}^{n,0} + \lambda \Delta \hat{\Gamma} = \sum_{\kappa} w_\kappa |\kappa; 0\rangle \langle \kappa; 0| + O(\lambda), \quad (8)$$

where $w_\kappa \equiv w_\kappa^0$ for $0 \leq \lambda < \delta$. In this case,

$$\mathcal{F}^\lambda[n] = \mathcal{T}_s[n] + \lambda \text{Tr}[\hat{\Gamma}^{n,0} \hat{W}] + O(\lambda^2). \quad (9)$$

Here, we have used $\text{Tr}[\hat{\Gamma}^{n,\lambda} \hat{T}] = \mathcal{T}_s[n] + O(\lambda^2)$, which follows from rewriting $\mathcal{T}_s \leq \text{Tr}[\hat{\Gamma}^{n,\lambda} \hat{T}]$ and

$\mathcal{F}^\lambda \leq \text{Tr}[\hat{\Gamma}^{n,0}(\hat{T} + \lambda\hat{W})]$ [from (5)] as $0 \leq \text{Tr}[\hat{\Gamma}^{n,\lambda} \hat{T}] - \mathcal{T}_s \leq \lambda \text{Tr}[(\hat{\Gamma}^{n,0} - \hat{\Gamma}^{n,\lambda}) \hat{W}]$ and letting $\lambda \rightarrow 0$. Thus,

$$\mathcal{E}_{\text{Hx}}[n] = \lim_{\lambda \rightarrow 0^+} \frac{\mathcal{F}^\lambda[n] - \mathcal{T}_s[n]}{\lambda} = \text{Tr}[\hat{\Gamma}^{n,0} \hat{W}] \quad (10)$$

follows straightforwardly. Clearly, when constraints \mathcal{C} allow only a pure state such that $\hat{\Gamma}^{n,0} = |\Phi_s\rangle \langle \Phi_s|$, we readily get

$$\mathcal{E}_{\text{Hx}}[n] = \langle \Phi_s | \hat{W} | \Phi_s \rangle \equiv E_{\text{Hx}}[n]$$

giving (2) for regular nonensemble theory. If, instead, $\hat{\Gamma}^{n,0} = w \sum_{\kappa} |\Phi_s^\kappa\rangle \langle \Phi_s^\kappa|$ for unique states $|\Phi_s^\kappa\rangle$, as in the case of an equiensemble $w_\kappa = w$, we end up with

$$\mathcal{E}_{\text{Hx}}[n] = w \sum_{\kappa} \langle \Phi_s^\kappa | \hat{W} | \Phi_s^\kappa \rangle, \quad (11)$$

where we purposely refrained from using common rewritings such as $\langle \Phi_s^\kappa | \hat{W} | \Phi_s^\kappa \rangle = E_{\text{Hx}}[\Phi_s^\kappa] = E_{\text{Hx}}[n_s^\kappa]$ to avoid the risk of confusion. Reference [24] reports details of several specialized examples of this type, including equiensembles over all members of a symmetry group.

Next, let us consider the case where we must account for degeneracies. Thus, for $\lambda \ll 1$, we write

$$|\kappa; \lambda\rangle = \sum_{\kappa'} U_{\kappa'\kappa} |\Phi^{\kappa'}\rangle + O(\lambda), \quad (12)$$

in which superpositions of different noninteracting Slater determinants $|\Phi^{\kappa}\rangle$ having the same kinetic energies and densities are allowed. The matrix \mathbb{U} is a unitary transformation that, regardless of the weights, leaves $\text{Tr}[\hat{\Gamma}_\mathbb{U} \hat{T}]$ and $\text{Tr}[\hat{\Gamma}_\mathbb{U} \hat{n}]$ unchanged for $\hat{\Gamma}_\mathbb{U} \equiv \sum_{\kappa} w_\kappa |\kappa; \lambda\rangle \langle \kappa; \lambda| = \sum_{\kappa\kappa_1\kappa_2} w_\kappa U_{\kappa_1\kappa} U_{\kappa_2\kappa}^* |\Phi^{\kappa_1}\rangle \langle \Phi^{\kappa_2}|$, using (12). However, $\text{Tr}[\hat{\Gamma}_\mathbb{U} \hat{W}] = \sum_{\kappa\kappa_1\kappa_2} w_\kappa U_{\kappa_1\kappa} U_{\kappa_2\kappa}^* \langle \Phi^{\kappa_1} | \hat{W} | \Phi^{\kappa_2} \rangle + O(\lambda)$ may change with \mathbb{U} . From the minimization of $\text{Tr}[\hat{\Gamma}^{n,\lambda}(\hat{T} + \lambda\hat{W})]$, we therefore get

$$\mathcal{E}_{\text{Hx}}[n] = \min_{\mathbb{U}} \text{Tr}[\hat{\Gamma}_\mathbb{U} \hat{W}], \quad (13)$$

which naturally incorporates multireference states, when appropriate (see the He example given just below).

Finally, to accommodate both the nondegenerate and degenerate cases that can arise simultaneously in Gross-Oliveira-Kohn [15–17] ensembles, we write the most general and amenable formula

$$\mathcal{E}_{\text{Hx}}[n] = \sum_{\kappa} w_\kappa \Lambda_{\text{Hx},\kappa}[n]. \quad (14)$$

Here, $\Lambda_{\text{Hx},\kappa}[n]$ are “block eigenvalues” of $\mathbb{W} \equiv \langle \Phi^{\kappa} | \hat{W} | \Phi^{\kappa'} \rangle$, obtained by diagonalizing submatrices \mathbb{W}^b (the blocks) of \mathbb{W} composed of states with the same kinetic energies and densities, and ordering the eigenvalues within each block while preserving the order of the blocks. Thus,

nondegenerate states correspond to blocks of one element, and the Hx energy of degenerate states is guaranteed minimized by the ordered eigenvalues because of the Schur-Horn theorem. A detailed proof of (14) is provided in Supplemental Material [30].

By way of example, consider the He atom in an excited state ensemble composed of the ground state $|0\rangle = |1s\downarrow 1s\uparrow\rangle$, and an arbitrary mix of the fourfold degenerate set of lowest excited single Slater determinants $|1\rangle = |1s\uparrow 2s\uparrow\rangle$, $|2\rangle = |1s\downarrow 2s\downarrow\rangle$, $|3\rangle = |1s\uparrow 2s\downarrow\rangle$, $|4\rangle = |1s\downarrow 2s\uparrow\rangle$. Previously reported work in Refs. [27–29] has identified and detailed how the correct spectra of the atom must be obtained by considering superpositions of Kohn-Sham determinants. Our goal in the following is merely to show that our approach includes such a result directly.

State $|0\rangle$ has particle density $n_0 = 2|\phi_{1s}|^2$ and kinetic energy $T_0 = 2t_{1s}$. States 1–4 all have the same density $n_\kappa = |\phi_{1s}|^2 + |\phi_{2s}|^2$ and kinetic energy $T_\kappa = t_{1s} + t_{2s}$. Here, $t_i = \langle i|\hat{t}|i\rangle$ is the single-particle kinetic energy of orbital i . We see that $\langle \kappa|\hat{n}|\kappa'\rangle$ and $\langle \kappa|\hat{T}|\kappa'\rangle$ are thus diagonal, with the exception of some elements that mix state 0 with states 1–4. We can therefore write

$$\hat{\Gamma}_U = w_0|0\rangle\langle 0| + \sum_{\kappa>0} w_\kappa|\kappa_U\rangle\langle \kappa_U| \in \mathcal{G}^{n,0}, \quad (15)$$

where $|\kappa_U\rangle = \sum_{1\leq\kappa'\leq 4} U_{\kappa'\kappa}|\kappa'\rangle$ for unitary matrix U on indices $1\leq\kappa, \kappa'\leq 4$.

For the ground state, we find $\Lambda_{\text{Hx},0} \equiv \langle 0|\hat{W}|0\rangle = (1s1s|1s1s)$. We now determine the block matrix $\langle \kappa|\hat{W}|\kappa'\rangle$ for $1\leq\kappa, \kappa'\leq 4$. The Slater-Condon rules give $W_{11} = W_{22} = (1s1s|2s2s) - (1s2s|1s2s) \equiv X - Y$ and $W_{33} = W_{44} = (1s1s|2s2s) \equiv X$. The only nonzero cross-terms are $\langle 3|\hat{W}|4\rangle = \langle 4|\hat{W}|3\rangle = -(1s2s|1s2s) = -Y$. Here $(ij|kl) = \frac{1}{2} \int d\mathbf{r}d\mathbf{r}' \phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\phi_k^*(\mathbf{r}')\phi_l(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$ is the usual two-electron-repulsion integral. Note that $0 \leq Y < X$. For this block, we find a threefold degenerate triplet eigenvalue $\Lambda_{\text{Hx},1T} = X - Y$ (with eigenstates $|\bar{1}/2\rangle = |1s\uparrow 2s\uparrow\rangle/|1s\downarrow 2s\downarrow\rangle$ and $|\bar{3}\rangle = [|1s\uparrow 2s\downarrow\rangle + |1s\downarrow 2s\uparrow\rangle]/\sqrt{2}$) and a higher energy singlet eigenvalue $\Lambda_{\text{Hx},2S} = X + Y$ (with eigenstate $|\bar{4}\rangle = [|1s\uparrow 2s\downarrow\rangle - |1s\downarrow 2s\uparrow\rangle]/\sqrt{2}$). Equation (14) then gives

$$\mathcal{E}_{\text{Hx}}[n] = w_0\Lambda_{\text{Hx},0} + w_T\Lambda_{\text{Hx},1T} + w_4\Lambda_{\text{Hx},2S}, \quad (16)$$

where $w_T = w_1 + w_2 + w_3$ and $w_4 = 1 - w_0 - w_T$. Finally, taking derivatives with respect to excited state weights w_T and w_4 as per Ref. [28] shows that a qualitatively correct excitation spectrum is obtained. By contrast, working directly at the level of $\text{Tr}[\hat{\Gamma}\hat{W}]$ within the restriction of single Slater determinants can lead to an alternative qualitatively incorrect result [28]. This case is automatically excluded by working within our setting.

We now proceed to work through another case, fully dissociated H_2 , exemplifying important size-consistency

considerations [31,32]. Unlike the He case above, we this time let the weights vary under two constraints: (i) the ensemble has only ground states, and (ii) neither atom has a magnetic moment. In a H_2 molecule at finite spacing, the four lowest KS states are [33]

$$\begin{aligned} |0\rangle &= |g\uparrow g\downarrow\rangle, & |1\rangle &= |u\uparrow g\downarrow\rangle, \\ |2\rangle &= |g\uparrow u\downarrow\rangle, & |3\rangle &= |u\uparrow u\downarrow\rangle. \end{aligned}$$

Here the gerade/ungerade molecular orbitals $|g/u\rangle = (1/\sqrt{2})(|a\rangle \pm |b\rangle)$ are built from localized atomic orbitals, $|a\rangle$ and $|b\rangle$, on atoms a and b , respectively. The states $|\kappa\rangle$, with $\kappa = 0, 1, 2, 3$ have been ordered according to their nondissociated energies but are degenerate in the dissociated limit considered here. The constraints allow a family of noninteracting “molecular” ensemble density matrices,

$$\hat{\Gamma}_{\text{mol}} = w_0|0\rangle\langle 0| + w_1|1\rangle\langle 1| + w_2|2\rangle\langle 2| + w_3|3\rangle\langle 3|, \quad (17)$$

where $\sum w_\kappa = 1$. Alternatively, we may take superpositions $|\bar{0}/\bar{1}\rangle = [|0\rangle \pm |1\rangle \mp |2\rangle - |3\rangle]/2$ of Kohn-Sham determinants $|0\rangle-|3\rangle$ to obtain localized states,

$$|\bar{0}\rangle = |a\uparrow b\downarrow\rangle, \quad |\bar{1}\rangle = |b\uparrow a\downarrow\rangle,$$

directly, and thus define a localized ensemble

$$\hat{\Gamma}_{\text{loc}} = \frac{1}{2}|\bar{0}\rangle\langle \bar{0}| + \frac{1}{2}|\bar{1}\rangle\langle \bar{1}|. \quad (18)$$

Both $\hat{\Gamma}_{\text{mol}}$ and $\hat{\Gamma}_{\text{loc}}$ are in $\mathcal{G}^{n,0}$ because they obey the constraints, provide the same ensemble particle density $n = n_a + n_b$, and have the same ensemble kinetic energy $\mathcal{T}_s[n] = \sum_\kappa w_\kappa T_\kappa = 2\langle a|\hat{t}|a\rangle = 2t_a$. But their action on the interaction operator \hat{W} is very different, leading to the nonuniqueness disaster if $\text{Tr}[\hat{\Gamma}\hat{W}]$ is applied directly. The result $\langle \kappa|\hat{W}|\kappa\rangle = (aa|aa)$ for all κ means that $\text{Tr}[\hat{\Gamma}_{\text{mol}}\hat{W}] = (aa|aa)$. By contrast, $\langle \bar{0}|\hat{W}|\bar{0}\rangle = \langle \bar{1}|\hat{W}|\bar{1}\rangle = 0$ gives $\text{Tr}[\hat{\Gamma}_{\text{loc}}\hat{W}] = 0$. It therefore follows that

$$\mathcal{E}_{\text{Hx}}[n] = \text{Tr}[\hat{\Gamma}_{\text{loc}}\hat{W}] = 0. \quad (19)$$

The main point here is the following: unless $\mathcal{G}^{n,0}$ is restricted to particular ensembles (e.g., $\hat{\Gamma}_{\text{mol}}$), $\mathcal{E}_{\text{Hx}}[n]$ is not affected by spurious interactions and, thus, size consistency at full dissociation is satisfied.

Finally, it should by now be apparent that we can summarize all previous results by writing

$$\mathcal{E}_{\text{Hx}}[n] = \min_{\hat{\Gamma} \in \mathcal{G}^{n,\lambda=0}} \text{Tr}[\hat{\Gamma}\hat{W}], \quad (20)$$

where we admit into $\mathcal{G}^{n,\lambda=0}$ all noninteracting ensembles of general form that simultaneously give the prescribed ensemble particle density n and exact Kohn-Sham kinetic energy $\mathcal{T}_s[n]$, and obey any additional constraints \mathcal{C} .

To conclude, in this work we have presented a Hartree-exchange functional [Eq. (3)] that is uniquely defined in ensemble density functional theory for a given set of constraints. In a more convenient form [Eq. (4)], it obviously avoids the nonuniqueness pathology, while preserving a maximal freedom from spurious interactions. The resulting Hartree-exchange functional $\mathcal{E}_{\text{Hx}}[n]$ reproduces special cases previously reported in the literature, including those requiring nontrivial superpositions of Kohn-Sham states [Eq. (13)], but can nonetheless straightforwardly be obtained via block diagonalization [Eq. (14)].

This work will thus aid in the development of future EDFT approximations along the lines of those previously considered [24,26,28,29,34–42], and will extend DFT to new physics. The approach can be applied to range-separated interactions to allow for cancellation of errors when combining with semilocal approximations. Equation (14) should help in tackling Fermionic systems where many states have the same density and kinetic energy (e.g., Hubbard models or cold atoms). With suitable generalization, this work may be extended to open systems, by noting that Eq. (3) depends only on the existence and continuity of $\mathcal{F}^\lambda[n]$ at $\lambda = 0$. Generalizations and approximations for the Hx and correlation functionals will be presented in future works—in particular, it will be interesting to gauge the importance of ghost-interaction leftovers.

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