‘Hartree-exchange’ in ensemble density functional theory: Avoiding the non-uniqueness 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 [equation (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-exchange in ensemble systems.

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 groundstates, 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,

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

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 $\rho_s(\mathbf{r}, \mathbf{r}') \rightarrow \text{Tr}[\hat{\Gamma}_0^n \hat{\rho}(\mathbf{r}, \mathbf{r}')] \text{ where } \hat{\Gamma}_0^n \text{ is the “ensemble density matrix” operator describing the reference Kohn-Sham state, and use } \text{Tr}[\hat{\Gamma}_0^n \hat{\rho}(\mathbf{r}, \mathbf{r})] = n(\mathbf{r}) \text{ to write}$

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

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 $\text{Tr}[\hat{\Gamma}_s^n \hat{W}]$ 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 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-exchange’ in EDFT has culminated with the proposal of a Symmetrized Eigenstate Hartree-exchange expression (SEHX) [27–29].

In this work, we put forward a universal and unifying treatment of the ‘Hartree-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 will 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 “non-uniqueness disaster”, and thus develop a functional which can be used directly or approximated for calculations.

We will show that a general approach free from pathologies follows directly from a definition of ‘Hartree-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 shall illustrate, Eq. (3) has several convenient corollaries [Eqs (10), (13), (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 non-interacting ensembles which 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 $\mathcal{E}_{\text{Hx}}$ 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 will come back on the following points by providing further details or explicit examples):

Avoidance of the non-uniqueness 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 non-uniqueness of $\hat{\Gamma} \rightarrow n$;

Maximal freedom from interactions: It is reassuring to note that avoiding the non-uniqueness disaster does not play against avoiding the spurious interactions we discussed above. This readily follow 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 shall first explore the derivation of, and consequences of this unifying picture of Hartree-exchange physics. Finally we will 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. *Firstly*, 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 groundstate $E_0 = \langle 0|\hat{H}|0\rangle$. The degenerate case above is, in fact, an important specialized version of this type of ensemble. For the sake of simplicity, we shall 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 non-trivial 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 and 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

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

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 $\mathcal{F}^\lambda$ 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

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

First, let us assume that there is a unique interacting ensemble $\hat{\Gamma}^{n,\lambda}$, which is connected perturbatively to a non-interacting one $\hat{\Gamma}^{n,0}$ along the adiabatic connection. Consider the case for which non-degenerate 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 non-ensemble 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. Ref. [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

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

in which superpositions of different non-interacting Slater determinants $|\Phi_s^{\kappa'}\rangle$ 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 $\hat{\Gamma}_\mathbb{U} \equiv \sum_\kappa w_\kappa |\kappa; \lambda\rangle \langle \kappa; \lambda| = \sum_{\kappa\kappa_1\kappa_2} w_\kappa U_{\kappa_1\kappa} U_{\kappa_2\kappa}^* |\Phi_s^{\kappa_1}\rangle \langle \Phi_s^{\kappa_2}|$, using (12). However, $\text{Tr}[\hat{\Gamma}_\mathbb{U} \hat{W}] = \sum_{\kappa\kappa_1\kappa_2} w_\kappa U_{\kappa_1\kappa} U_{\kappa_2\kappa}^* \langle \Phi_s^{\kappa_1} | \hat{W} | \Phi_s^{\kappa_2} \rangle + O(\lambda)$ 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 multi-reference states, when appropriate (see the He example given just below).

Finally, to accommodate both the non-degenerate and degenerate cases that can arise simultaneously in Gross, Oliveira and 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 $\mathbb{W} \equiv \langle \Phi_s^\kappa | \hat{W} | \Phi_s^{\kappa'} \rangle$, 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 whilst preserving the order of the blocks. Thus, non-degenerate 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 the Supplemental Material[30].

By way of example, consider the He atom in an excited state ensemble composed of the groundstate $|0\rangle = |1s\downarrow 1s\uparrow\rangle$, and an arbitrary mix of the a 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 which mix state 0 with states 1-4. We can therefore write

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

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

For the groundstate, 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 non-zero cross-terms are $\langle 3|\hat{W}|4\rangle = \langle 4|\hat{W}|3\rangle = -(1s2s|1s2s) = -Y$. Here $\langle ij|kl\rangle = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) \phi_k^*(\mathbf{r}') \phi_l(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$ is the usual two-electron-repulsion integral. Note that $0 \leq Y < X$. For this block, we find a three-fold 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 $|\bar{4}\rangle = [|1s\uparrow 2s\downarrow\rangle - |1s\downarrow 2s\uparrow\rangle] / \sqrt{2}$). Eq. (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 spectra 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 alternative qualitatively incorrect result[28]. This case is *automatically excluded* by working within our setting.

We shall now proceed to work through another case: *fully dissociated* H_2 , exemplifying important size-consistency considerations[31, 32]. Unlike the He case above, we will this time let the weights vary under two constraints: i) the ensemble has only groundstates, ii) neither atom has a magnetic moment. In an H_2 molecule at finite spacing, the four lowest KS states are[33]

$$|0\rangle = |g\uparrow g\downarrow\rangle, |1\rangle = |u\uparrow g\downarrow\rangle, |2\rangle = |g\uparrow u\downarrow\rangle, |3\rangle = |u\uparrow u\downarrow\rangle.$$

Here the *gerade/ungerade* molecular orbitals $|g/u\rangle = \frac{1}{\sqrt{2}} [|a\rangle \pm |b\rangle]$ 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 *non-dissociated* energies but are degenerate in the

dissociated limit considered here. The constraints allow a family of non-interacting “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,

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

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 $\mathcal{T}_s = \sum_\kappa w_\kappa T_\kappa = 2\langle a|\hat{t}|a\rangle = 2t_a$. But their action on the interaction operator $\hat{W}$ is very different, leading to the non-uniqueness 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 non-interacting 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 non-uniqueness 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 non-trivial superpositions of Kohn-Sham states [Eq. (13)], but can nonetheless straightforwardly be obtained via block diagonalisation [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 $\hat{W} \rightarrow \hat{W}^{\text{sr/lr}}$ to allow for cancellation of errors when combining with semi-local approximations. Eq. (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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Supplementary material for “ ‘Hartree-exchange’ in ensemble density functional theory: Avoiding the non-uniqueness disaster ”

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We provide the proof for Eq. (14) of the main text using the Schur-Horn theorem.

ESTABLISHING EQ. (14) IN THE MANUSCRIPT

The role of eigenvalues

We begin by considering the case of a set of Kohn-Sham states that are degenerate on $\hat{T}$ and $\hat{n}$ but not necessarily on $\hat{W}$. Therefore, as stated in the main text, we seek $\mathbb{U}$ that minimizes

$$\text{Tr} [\hat{\Gamma}_{\mathbb{U}} \hat{W}] = \text{Tr} [\mathbb{G} \mathbb{W}^{\mathbb{U}}], \quad \mathbb{W}^{\mathbb{U}} = \mathbb{U} \mathbb{W} \mathbb{U}^{\dagger}; \quad (1)$$

where $\mathbb{G}$ is a diagonal matrix with the relevant (non-negative) weights w_{κ} pre-assigned in non-increasing order, $\mathbb{U}$ is any unitary transformation, and $\mathbb{W}$ is the matrix with elements $\langle \kappa | \hat{W} | \kappa' \rangle$ with respect to the aforementioned states.

We will now prove that

$$\min_{\mathbb{U}} \text{Tr} [\mathbb{G} \mathbb{W}^{\mathbb{U}}] = \sum_{\kappa} w_{\kappa} \Lambda_{\kappa} \quad (2)$$

where Λ_{κ} are the eigenvalues of $\mathbb{W}$ taken in non-decreasing order.

To begin, we introduce $q_j = w_j - w_{j+1} \geq 0$, such that $w_{\kappa} = \sum_{j \geq \kappa} q_j$. For systems with a finite number of non-zero weights, like the ones considered in the manuscript, we have $w_{\kappa > \kappa_m} = 0$ and thus $q_{j > \kappa_m} = 0$ for some state $|\kappa_m\rangle$, which terminates the sums. Therefore, we can write

$$\begin{aligned} \text{Tr} [\mathbb{G} \mathbb{W}^{\mathbb{U}}] &= \sum_{\kappa} w_{\kappa} W_{\kappa\kappa}^{\mathbb{U}} = \sum_{\kappa} \sum_{j \geq \kappa} q_j W_{\kappa\kappa}^{\mathbb{U}} \\ &= \sum_j q_j \text{Tr}_j [\mathbb{W}^{\mathbb{U}}] \end{aligned} \quad (3)$$

where $\text{Tr}_j [\mathbb{W}^{\mathbb{U}}] = \sum_{\kappa \leq j} W_{\kappa\kappa}^{\mathbb{U}}$ is the partial trace on the matrix $\mathbb{W}^{\mathbb{U}}$ and we used $\sum_{\kappa} \sum_{j \geq \kappa} a_{jk} \equiv \sum_j \sum_{\kappa \leq j} a_{jk}$.

The proof of Eq. (2) relies on two steps: 1) For any given matrix $\mathbb{W}^{\mathbb{U}}$ the matrix $\mathbb{W}^{\mathbb{U}'}$ with the same diagonal elements ordered in non-decreasing fashion (e.g. as obtained by using elementary interchange transformations) gives $\text{Tr}_j [\mathbb{W}^{\mathbb{U}}] \geq \text{Tr}_j [\mathbb{W}^{\mathbb{U}'}], \forall j$. 2) For any matrix $\mathbb{W}^{\mathbb{U}'}$ with non-decreasing elements down the diagonal, the matrix $\mathbb{W}^{\mathbb{V}}$ which is diagonal with non-decreasing eigenvalues down the diagonal obeys $\text{Tr}_j [\mathbb{W}^{\mathbb{U}'}] \geq \text{Tr}_j [\mathbb{W}^{\mathbb{V}}], \forall j$ because of the Schur-Horn theorem.

For 1), we proceed by induction. Given a set of diagonal elements $\{d\}$, it is clear that $\text{Tr}_0 [\{d\}] = d_0$ is minimized by choosing the smallest possible value for $d_0 \in \{d\}$. Then $\text{Tr}_1 [\{d\}] = \text{Tr}_0 [\{d\}] + d_1 = d_0 + d_1$ must be minimized by choosing the smallest remaining element. And so on until the list is exhausted. Thus, for any given matrix $\mathbb{U}$, the partial traces are made smallest by choosing the related matrix $\mathbb{W}^{\mathbb{U}'}$ with non-decreasing diagonal elements.

The Schur-Horn theorem provides the proof of 2). It gives (see Appendix A) that for non-decreasing Λ_k and M_{kk} , $\sum_{k \leq j} \Lambda_k \leq \sum_{k \leq j} M_{kk}$. Here M_{kk} are diagonal elements of an Hermitian matrix $\mathbb{M}$ with eigenvalues Λ_k . This accounts for our case, since all the considered matrices are similar to one another by construction and, thus, must share the same set of eigenvalues.

Putting it all together and using (3), we get the identities

$$\begin{aligned} \min_{\mathbb{U}} \text{Tr} [\mathbb{G} \mathbb{W}^{\mathbb{U}}] &= \min_{\mathbb{U}} \sum_j q_j \text{Tr}_j [\mathbb{W}^{\mathbb{U}}] = \sum_j q_j \text{Tr}_j [\mathbb{W}^{\mathbb{V}}] \\ &= \sum_j q_j \sum_{\kappa \leq j} \Lambda_{\kappa} = \sum_{\kappa} w_{\kappa} \Lambda_{\kappa}, \end{aligned}$$

because diagonalizing $\mathbb{W}$ by organizing the eigenvalues in the described order is one of the possible unitary transformations (here called $\mathbb{V}$) that can be performed. Thus, Eq. (2) holds true.

The role of “block eigenvalues”

More commonly, we will have to deal with a mixture of non-degenerate and degenerate states. In this more general case, it remains to specify that Λ_{κ} are ordered “block eigenvalues” of $\mathbb{W}$, that is eigenvalues of a series of matrices $\mathbb{W}^b$ determined from the structure of

$$[\mathbb{T}]_{\kappa_1 \kappa_2} = \langle \Phi^{\kappa_1} | \hat{T} | \Phi^{\kappa_2} \rangle, \quad (4)$$

and later arranged in correspondence with the weights.

Algorithmically, we proceed as follows:

1. We compute $\mathbb{T}$ whose structure is determined (up to trivial rearrangement of degenerate states) by the Kohn-Sham reference system. Along the diagonal, we seek the largest possible blocks $\mathcal{B}^b$ of dimension

$N^b \times N^b$ for which $T_{\kappa_1 \kappa_2} = T^b \delta_{\kappa_1 \kappa_2}$ is a constant T^b times the identity matrix within the block. *Note, the ordering of these blocks must be preserved in subsequent steps.*

We illustrate such a matrix below for the case of three blocks,

$$\mathbb{T} = \begin{pmatrix} \boxed{T_{00}} & \times & \times & \times & \times & \times & \times \\ \times & \boxed{T_{11}} & 0 & 0 & 0 & \times & \times \\ \times & 0 & \boxed{T_{22}} & 0 & 0 & \times & \times \\ \times & 0 & 0 & \boxed{T_{33}} & 0 & \times & \times \\ \times & 0 & 0 & 0 & \boxed{T_{44}} & \times & \times \\ \times & \times & \times & \times & \times & \boxed{T_{55}} & 0 \\ \times & \times & \times & \times & \times & 0 & \boxed{T_{66}} \end{pmatrix}.$$

Here the three blocks $\mathcal{B}^1$, $\mathcal{B}^2$ and $\mathcal{B}^3$ have $N^1 = 1$, $N^2 = 4$ and $N^3 = 2$ with block kinetic energies $T^1 = T_{00}$, $T^2 = T_{11} = T_{22} = T_{33} = T_{44}$ and $T^3 = T_{55} = T_{66}$.

- Next, we identify the corresponding blocks $\mathcal{B}^b$ in $\mathbb{W}$ and calculate the “block eigenvalues” Λ_ξ^b of the matrix $\mathbb{W}^b$ defined on elements in $\mathcal{B}^b$ only. We label these eigenvalue Λ_ξ by an index $0 \leq \xi < N^b$, and order them non-decreasingly, within each block.

We show below the blocks $\mathbb{W}^1$, $\mathbb{W}^2$ and $\mathbb{W}^3$ corresponding to $\mathbb{T}$ above,

$$\mathbb{W} = \begin{pmatrix} \boxed{\mathbb{W}^1} & \times & \times & \times & \times & \times & \times \\ \times & & & & & & \\ \times & & \boxed{\mathbb{W}^2} & & & & \\ \times & & & & & & \\ \times & & & & & & \\ \times & \times & \times & \times & \times & \boxed{\mathbb{W}^3} & \\ \times & \times & \times & \times & \times & & \end{pmatrix}.$$

These are then diagonalized separately to obtain $\{\Lambda_0^1\}$, $\{\Lambda_0^1, \Lambda_1^1, \Lambda_2^1, \Lambda_3^1\}$ and $\{\Lambda_0^3, \Lambda_1^3\}$, respectively for $\mathbb{W}^1$, $\mathbb{W}^2$ and $\mathbb{W}^3$.

- Finally, taking the blocks in their original order, we perform the weighted sum

$$\mathcal{E}_{\text{Hx}}[n] = \sum_b \sum_{0 \leq \xi < N^b} w_{\kappa^b + \xi} \Lambda_\xi^b \quad (5)$$

where $\kappa^b = \sum_{b' < b} N^{b'}$ labels the first element of block $\mathcal{B}^b$, and Λ_ξ^b is the ξ th eigenvalue of $\mathbb{W}^b$. Here we use the results from the previous section within each block (where degenerate perturbation theory allows unitary transformations), but not between blocks (which non-degenerate perturbation theory forbids mixing). *It is important to note that neighbouring elements from different blocks can decrease in value even if κ increases.*

Finally, from Eq. (5) we arrive at Eq. (14) of the main text by simply stressing the energy meaning

of the aforementioned block eigenvalues as well as their functional dependency on the overall ensemble particle density

$$\mathcal{E}_{\text{Hx}}[n] = \sum_{\kappa} w_{\kappa} \Lambda_{\text{Hx}, \kappa}[n] \quad (6)$$

i.e., we have renamed/relabelled $\kappa^b + \xi \rightarrow \kappa$ and $\Lambda_\xi^b \rightarrow \Lambda_{\text{Hx}, \kappa}[n]$. As elsewhere, all functionals of n also depend on our choice of constraints $\mathcal{C}$.

In our example this is,

$$\begin{aligned} \mathcal{E}_{\text{Hx}}[n] &= [w_0 \Lambda_0^1] \\ &\quad + [w_1 \Lambda_0^2 + w_2 \Lambda_1^2 + w_3 \Lambda_2^2 + w_4 \Lambda_3^2] \\ &\quad + [w_5 \Lambda_0^3 + w_6 \Lambda_1^3] \\ &\equiv \sum_{\kappa} w_{\kappa} \Lambda_{\text{Hx}, \kappa}[n]. \end{aligned}$$

Here, Λ_0^2 can potentially be smaller than Λ_0^1 (similarly for Λ_0^3 and Λ_3^2) due to the block structure.

Appendix A: Schur-Horn corollary

Commonly, the Schur-Horn theorem is written with partial sums of non-increasing elements which obey

$$\sum_{k \leq j} M_{kk} \leq \sum_{k \leq j} \Lambda_k, \quad \sum_{k \leq N} M_{kk} = \sum_{k \leq N} \Lambda_k = \text{Tr}[\mathbb{M}],$$

where M_{kk} are the diagonal elements of matrix $\mathbb{M}$ and Λ_k are its eigenvalues. See e.g. the Wikipedia entry at https://en.wikipedia.org/wiki/Schur%E2%80%9993Horn_theorem.

The version employed here is a direct corollary, as shall be shown below. Firstly, we set $M'_{kk} = M_{(N-k)(N-k)}$ and $\Lambda'_k = \Lambda_{N-k}$ to reverse the order so that elements are non-decreasing. This gives,

$$\sum_{j' < k \leq N} M'_{kk} \leq \sum_{j' < k \leq N} \Lambda'_k, \quad \sum_{k \leq N} M'_{kk} = \sum_{k \leq N} \Lambda'_k = \text{Tr}[\mathbb{M}],$$

for non-decreasing elements and $j' + 1 = N - j$.

We then write $\sum_{k \leq j} M_{kk} + \sum_{j < k \leq N} M_{kk} = \sum_{k \leq N} M_{kk} = \text{Tr}[\mathbb{M}]$ and $\sum_{k \leq j} \Lambda_k + \sum_{j < k \leq N} \Lambda_k = \sum_{k \leq N} \Lambda_k = \text{Tr}[\mathbb{M}]$ (where we drop primes and used the invariance of the trace). Therefore,

$$0 \geq \sum_{j < k \leq N} M_{kk} - \sum_{j < k \leq N} \Lambda_k = \sum_{k \leq j} \Lambda_k - \sum_{k \leq j} M_{kk}$$

and, finally, we get the desired

$$\sum_{k \leq j} \Lambda_k \leq \sum_{k \leq j} M_{kk}.$$