

# Individual correlations in ensemble density-functional theory: State-driven/density-driven decomposition without additional Kohn–Sham systems

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Gould and Pittalis [Phys. Rev. Lett. 123, 016401 (2019)] recently revealed a density-driven correlation energy in many-electron ensembles that must be accounted for by approximations. We show that referring to auxiliary state-driven Kohn–Sham (KS) systems, which was inherent to its evaluation, is in fact not needed. Instead, individual-state densities can be extracted directly from the KS ensemble. On that basis, a simpler and more general expression is derived and tested. The importance of density-driven effects is thus confirmed, and a direct route to approximations is introduced.

*Introduction.* Time-dependent density-functional theory (TD-DFT) [1] has become over the last two decades the method of choice for modeling properties of electronically-excited molecules and materials. Despite this success, which is explained by the moderate computational cost of the method, TD-DFT still suffers from various deficiencies. The latter drastically reduce its applicability, in particular to a large variety of molecules and materials where electron correlation is strong [2]. These failures originate from the single-reference perturbative character of the theory [in the widely used linear response regime] and the common adiabatic approximation, where memory effects are absent. As a result, the interest in *time-independent* formulations of DFT for excited states has increased substantially over the last decade [3–24].

Gross–Oliveira–Kohn (GOK) ensemble DFT [25–27], which is a generalization of Theophilou’s DFT for equiensembles [28, 29], is one of these (low-cost) alternatives. Unlike state-averaged quantum chemical methods [30], GOK-DFT describes (in principle exactly) each state that belong to the ensemble with a single Slater determinant (or a configuration state function), in analogy with regular ground-state Kohn–Sham (KS) DFT. A substantial difference with the latter though is that, in GOK-DFT, the non-interacting KS ensemble is expected to reproduce the true interacting ensemble density [i.e. the weighted sum of ground- and excited-state densities] only, not each individual (ground- or excited-state) density. This subtle point, which has not been much emphasized in the literature until very recently [31, 32], is central in the Gould–Pittalis correlation energy decomposition into state-driven (SD) and density-driven (DD) contributions [31].

This decomposition shed a new light on individual correlations within an ensemble and is relevant to the design of density-functional approximations for ensembles, which is an important outstanding problem in DFT [11, 17, 24, 33]. The way such a decomposition should be written and implemented is, however, open to discussion. Gould and Pittalis [31] proposed to introduce

state-specific KS systems (one for each state, in addition to the KS ensemble) which are expected to reproduce the exact individual-state densities. While KS potentials for excited states are well defined for Coulomb systems [34–36], their construction is not straightforward in the general case. When they exist, the non-uniqueness problem can be solved through a selection procedure [31]. But there might also be situations where such potentials do not exist. A simple example is given by the two-electron asymmetric Hubbard dimer [37] where the occupation of the atomic sites plays the role of the density. In the non-interacting dimer, the density of the first singlet excited state does not vary with the KS potential. It matches the interacting excited-state density only when the dimer is symmetric [14].

As shown in this Letter, the non-uniqueness or non-existence of excited-state KS potentials is not a problem as such in the context of ensemble DFT, where the KS potential is well defined (up to a constant) [26], simply because individual-state densities can be extracted in principle exactly from the KS density-functional ensemble. On that basis, an exact expression for the individual density-functional correlation energies and their subsequent SD/DD decomposition is derived. While being simpler and more general (i.e. applicable to all systems) than the Gould–Pittalis decomposition [31], it uncovers the relation between individual and ensemble correlations, thus offering a clearer way to practical approximations.

*A brief review of GOK-DFT.* Let us consider the  $M+1$  lowest (in energy) solutions to the electronic Schrödinger equation  $\hat{H}\Psi_I = E_I\Psi_I$ ,  $0 \leq I \leq M$ , where the Hamiltonian  $\hat{H} = \hat{T} + \hat{W}_{ee} + \hat{V}_{\text{ext}}$  is the sum of the  $N$ -electron kinetic energy, Coulomb repulsion, and local multiplicative external potential  $\hat{V}_{\text{ext}} \equiv \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i) \times$  operators, respectively. For simplicity, we will assume that the energies are not degenerate, i.e.  $E_0 < E_1 < \dots < E_M$ . Note that the theory can be easily extended to multiplets by assigning the same ensemble weight to degenerate states [26]. The ensemble energy  $E^{\mathbf{w}} = \sum_{I=0}^M \mathbf{w}_I E_I$  is a

weighted sum of ground- and excited-state energies where the (positive) ensemble weights decrease with increasing index  $I$ . They are normalized, i.e.  $\mathbf{w}_0 = 1 - \sum_{I=1}^M \mathbf{w}_I$ , so that only the weights assigned to the excited states  $\mathbf{w} \equiv (\mathbf{w}_1, \mathbf{w}_2, \dots, \mathbf{w}_M)$  are allowed to vary *independently*. In GOK-DFT, the ensemble energy is determined as follows for given and fixed weights  $\mathbf{w}$  [26]:

$$E^{\mathbf{w}} = \min_{\{\varphi_k\}_k} \left\{ \text{Tr} \left[ \hat{\gamma}^{\mathbf{w}} \left( \hat{T} + \hat{V}_{\text{ext}} \right) \right] + E_{\text{Hxc}}^{\mathbf{w}}[n_{\hat{\gamma}^{\mathbf{w}}}] \right\}, \quad (1)$$

where  $\text{Tr}$  denotes the trace,  $\hat{\gamma}^{\mathbf{w}} = \sum_{I=0}^M \mathbf{w}_I |\Phi_I\rangle \langle \Phi_I|$ , and  $n_{\hat{\gamma}^{\mathbf{w}}}(\mathbf{r}) \equiv \sum_{I=0}^M \mathbf{w}_I n_{\Phi_I}(\mathbf{r})$  is a trial ensemble density. The trial determinants (or configuration state functions)  $\Phi_I$  are all generated from the same set  $\{\varphi_k\}_k$  of orthonormal molecular orbitals that are optimized variationally. The ensemble Hartree-exchange-correlation (Hxc) density functional in Eq. (1) can be decomposed exactly as follows:

$$E_{\text{Hxc}}^{\mathbf{w}}[n] = E_{\text{Hx}}^{\mathbf{w}}[n] + E_{\text{c}}^{\mathbf{w}}[n], \quad (2)$$

where the Hx ensemble functional [12]

$$E_{\text{Hx}}^{\mathbf{w}}[n] = \sum_{K=0}^M \mathbf{w}_K \langle \Phi_K^{\mathbf{w}}[n] | \hat{W}_{\text{ee}} | \Phi_K^{\mathbf{w}}[n] \rangle \quad (3)$$

is obtained from the KS ensemble that reproduces the density  $n$ :

$$\sum_{K=0}^M \mathbf{w}_K n_{\Phi_K^{\mathbf{w}}[n]}(\mathbf{r}) = n(\mathbf{r}). \quad (4)$$

Note that, in the general case, the  $N$ -electron KS wavefunctions  $\{\Phi_K^{\mathbf{w}}[n]\}_{0 \leq K \leq M}$  can be configuration state functions [12], i.e. linear combinations of KS determinants. They are in principle weight-dependent so that the density  $n$  can be reproduced, whatever the value of the ensemble weights [7, 14]. The minimizing KS wavefunctions  $\{\Phi_I^{\mathbf{w}} \equiv \Phi_I^{\mathbf{w}}[n^{\mathbf{w}}]\}_{0 \leq I \leq M}$  in Eq. (1) reproduce the exact ensemble density  $n^{\mathbf{w}}$ :

$$\sum_{I=0}^M \mathbf{w}_I n_{\Phi_I^{\mathbf{w}}}(\mathbf{r}) = \sum_{I=0}^M \mathbf{w}_I n_{\Psi_I}(\mathbf{r}) \equiv n^{\mathbf{w}}(\mathbf{r}), \quad (5)$$

so that the exact ensemble energy can be expressed as

$$E^{\mathbf{w}} = \sum_{I=0}^M \mathbf{w}_I \langle \Phi_I^{\mathbf{w}} | \hat{T} + \hat{V}_{\text{ext}} | \Phi_I^{\mathbf{w}} \rangle + E_{\text{Hxc}}^{\mathbf{w}}[n^{\mathbf{w}}]. \quad (6)$$

The corresponding minimizing orbitals fulfill the ensemble KS equations [26],

$$\left[ -\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{Hxc}}^{\mathbf{w}}[n^{\mathbf{w}}](\mathbf{r}) \right] \varphi_p^{\mathbf{w}}(\mathbf{r}) = \varepsilon_p^{\mathbf{w}} \varphi_p^{\mathbf{w}}(\mathbf{r}), \quad (7)$$

where  $v_{\text{Hxc}}^{\mathbf{w}}[n](\mathbf{r}) = \delta E_{\text{Hxc}}^{\mathbf{w}}[n] / \delta n(\mathbf{r})$  is the ensemble Hxc density-functional potential. Note that, when the KS

wavefunctions are single determinants [we make this assumption in the following, for simplicity], their density can be expressed as follows:

$$n_{\Phi_I^{\mathbf{w}}}(\mathbf{r}) = \sum_p \theta_p^I |\varphi_p^{\mathbf{w}}(\mathbf{r})|^2, \quad (8)$$

where  $\theta_p^I$  is the (fixed and integer) occupation number of the orbital  $\varphi_p^{\mathbf{w}}$  in the determinant  $\Phi_I^{\mathbf{w}}$ .

*Extracting exact individual densities.* As pointed out in Ref. [31], Eq. (5) does not imply that the KS wavefunctions reproduce the exact individual densities  $\{n_{\Psi_I}\}_{0 \leq I \leq M}$ . Nevertheless, these densities can be extracted directly from the KS ensemble, as we will see. This means that it is in principle not necessary to refer to additional state-specific KS systems for modeling individual-state properties within an ensemble.

We start from the simple observation that, like the energy [24], the density of any (ground or excited) state can be extracted from the (linear-in- $\mathbf{w}$ ) ensemble density as follows:

$$\begin{aligned} n_{\Psi_J}(\mathbf{r}) &= n_{\Psi_0}(\mathbf{r}) + \sum_{I=1}^M \delta_{IJ} \left( n_{\Psi_I}(\mathbf{r}) - n_{\Psi_0}(\mathbf{r}) \right) \\ &= n^{\mathbf{w}}(\mathbf{r}) - \sum_{I=1}^M \mathbf{w}_I \frac{\partial n^{\mathbf{w}}(\mathbf{r})}{\partial \mathbf{w}_I} + \sum_{I=1}^M \delta_{IJ} \frac{\partial n^{\mathbf{w}}(\mathbf{r})}{\partial \mathbf{w}_I} \\ &= n^{\mathbf{w}}(\mathbf{r}) + \sum_{I=1}^M (\delta_{IJ} - \mathbf{w}_I) \frac{\partial n^{\mathbf{w}}(\mathbf{r})}{\partial \mathbf{w}_I}. \end{aligned} \quad (9)$$

By inserting the KS ensemble density expression of Eq. (5) into Eq. (9) we can express the exact deviation in density [that we will refer to as *DD effect*] of the true interacting state from the KS one as follows:

$$n_{\Psi_J}(\mathbf{r}) - n_{\Phi_J^{\mathbf{w}}}(\mathbf{r}) = \sum_{I=1}^M \sum_{K=0}^M (\delta_{IJ} - \mathbf{w}_I) \mathbf{w}_K \frac{\partial n_{\Phi_K^{\mathbf{w}}}(\mathbf{r})}{\partial \mathbf{w}_I}, \quad (10)$$

where, as readily seen, the key quantity to model is the linear response  $\partial n_{\Phi_K^{\mathbf{w}}}(\mathbf{r}) / \partial \mathbf{w}_I = 2 \sum_p \theta_p^K \varphi_p^{\mathbf{w}}(\mathbf{r}) \partial \varphi_p^{\mathbf{w}}(\mathbf{r}) / \partial \mathbf{w}_I$  [we use real algebra for simplicity] of the individual KS densities to variations in the ensemble weights. In the following we denote  $i$  (or  $j$ ) the orbitals that are occupied in the ensemble, i.e. those that fulfill  $\sum_{K=0}^M \mathbf{w}_K \theta_i^K > 0$ . Unoccupied orbitals will be denoted as  $a$ . According to Eq. (7) and first-order perturbation theory, the response of the occupied KS orbitals reads

$$\frac{\partial \varphi_i^{\mathbf{w}}(\mathbf{r})}{\partial \mathbf{w}_I} = \sum_a \frac{\langle \varphi_a^{\mathbf{w}} | \hat{V}_{\text{Hxc}, \mathbf{w}_I}^{\mathbf{w}} | \varphi_i^{\mathbf{w}} \rangle}{\varepsilon_i^{\mathbf{w}} - \varepsilon_a^{\mathbf{w}}} \varphi_a^{\mathbf{w}}(\mathbf{r}), \quad (11)$$

where the local multiplicative perturbation operator

$\hat{\mathcal{V}}_{\text{Hxc},\mathbf{w}_I}^{\mathbf{w}} \equiv \mathcal{V}_{\text{Hxc},\mathbf{w}_I}^{\mathbf{w}}(\mathbf{r}) \times$  is defined as follows:

$$\mathcal{V}_{\text{Hxc},\mathbf{w}_I}^{\mathbf{w}}(\mathbf{r}) = \frac{d}{d\mathbf{w}_I} \left[ v_{\text{Hxc}}^{\mathbf{w}}[n^{\mathbf{w}}](\mathbf{r}) \right] = \left. \frac{\partial v_{\text{Hxc}}^{\mathbf{w}}[n^{\boldsymbol{\xi}}](\mathbf{r})}{\partial \mathbf{w}_I} \right|_{\boldsymbol{\xi}=\mathbf{w}} + \int d\mathbf{r}' \frac{\delta v_{\text{Hxc}}^{\mathbf{w}}[n^{\mathbf{w}}](\mathbf{r})}{\delta n(\mathbf{r}')} \frac{\partial n^{\mathbf{w}}(\mathbf{r}')}{\partial \mathbf{w}_I}. \quad (12)$$

Note that, like in linear response TD-DFT [2], the perturbation depends on the response of the KS orbitals through the ensemble Hxc kernel contribution [last term on the right-hand side of Eq. (12)]. By expressing the response  $\partial n^{\mathbf{w}}(\mathbf{r})/\partial \mathbf{w}_I$  of the ensemble density in terms of the KS orbitals and their first-order derivatives [see Eqs. (5) and (8)], we finally obtain the following *static* linear response equations:

$$\begin{aligned} \frac{\partial \varphi_i^{\mathbf{w}}(\mathbf{r})}{\partial \mathbf{w}_I} &= \sum_a \frac{\varphi_a^{\mathbf{w}}(\mathbf{r})}{\varepsilon_i^{\mathbf{w}} - \varepsilon_a^{\mathbf{w}}} \int d\mathbf{r}' \mathcal{V}_{\text{Hxc},I}^{\mathbf{w}}(\mathbf{r}') \varphi_i^{\mathbf{w}}(\mathbf{r}') \varphi_a^{\mathbf{w}}(\mathbf{r}') \\ &+ 2 \sum_a \sum_j \sum_{K=0}^M \frac{\mathbf{w}_K \theta_j^K \varphi_a^{\mathbf{w}}(\mathbf{r})}{\varepsilon_i^{\mathbf{w}} - \varepsilon_a^{\mathbf{w}}} \int d\mathbf{r}' \int d\mathbf{r}'' \frac{\delta v_{\text{Hxc}}^{\mathbf{w}}[n^{\mathbf{w}}](\mathbf{r}')}{\delta n(\mathbf{r}'')} \\ &\times \varphi_i^{\mathbf{w}}(\mathbf{r}') \varphi_a^{\mathbf{w}}(\mathbf{r}') \varphi_j^{\mathbf{w}}(\mathbf{r}'') \frac{\partial \varphi_j^{\mathbf{w}}(\mathbf{r}'')}{\partial \mathbf{w}_I}, \end{aligned} \quad (13)$$

where

$$\begin{aligned} \mathcal{V}_{\text{Hxc},I}^{\mathbf{w}}(\mathbf{r}) &= \left. \frac{\partial v_{\text{Hxc}}^{\mathbf{w}}[n^{\boldsymbol{\xi}}](\mathbf{r})}{\partial \mathbf{w}_I} \right|_{\boldsymbol{\xi}=\mathbf{w}} \\ &+ \sum_p (\theta_p^I - \theta_p^0) \int d\mathbf{r}' \frac{\delta v_{\text{Hxc}}^{\mathbf{w}}[n^{\mathbf{w}}](\mathbf{r}')}{\delta n(\mathbf{r}')} |\varphi_p^{\mathbf{w}}(\mathbf{r}')|^2 \end{aligned} \quad (14)$$

is what remains from the full perturbation in Eq. (12) when the true densities are approximated by the KS ones. As readily seen from Eq. (13), this part of the perturbation ignites the response of the KS orbitals which should then be updated (*via* the ensemble Hxc kernel contribution) until a self-consistent convergence is reached. Note that, for practical purposes, one should rewrite Eq. (13) as a coupled-perturbed equation, by analogy with Ref. [38]. If the exact ensemble potential and kernel were known, one should ultimately recover the exact linear response, thus leading to the true individual densities *via* Eq. (10). This is the first key result of this work. Note that DD effects can still be (partially) described by means of Eq. (13) even if the simple (weight-independent) ground-state functional approximation  $E_{\text{Hxc}}^{\mathbf{w}}[n] \approx E_{\text{Hxc}}[n]$  [15, 39] is employed. Indeed, in the latter case, the first term on the right-hand side of Eq. (14) vanishes but not the second one that involves the conventional ground-state Hxc kernel  $\delta v_{\text{Hxc}}[n](\mathbf{r})/\delta n(\mathbf{r}')$ .

*Individual Hxc energies.* The next natural step consists in extracting individual Hxc density-functional energies from the KS ensemble. For that purpose, we use the analog of Eq. (9) for energies [24] which, when combined with the *variational* KS expression of the ensemble energy

in Eqs. (1) and (6), leads to the following exact (ground- and excited-state) energy level expressions:

$$E_J = \langle \Phi_J^{\mathbf{w}} | \hat{T} + \hat{V}_{\text{ext}} | \Phi_J^{\mathbf{w}} \rangle + E_{\text{Hxc},J}^{\mathbf{w}}[n^{\mathbf{w}}], \quad (15)$$

where the ensemble-density-functional *individual* Hxc energy reads

$$\begin{aligned} E_{\text{Hxc},J}^{\mathbf{w}}[n] &= E_{\text{Hxc}}^{\mathbf{w}}[n] + \sum_{I=1}^M (\delta_{IJ} - \mathbf{w}_I) \frac{\partial E_{\text{Hxc}}^{\mathbf{w}}[n]}{\partial \mathbf{w}_I} \\ &+ \int d\mathbf{r} \frac{\delta E_{\text{Hxc}}^{\mathbf{w}}[n]}{\delta n(\mathbf{r})} (n_{\Phi_J^{\mathbf{w}}}(\mathbf{r}) - n(\mathbf{r})). \end{aligned} \quad (16)$$

Note that, as expected, the ensemble density-functional Hxc energy is recovered from the weighted sum of the individual Hxc components [see Eqs. (4) and (16)]:

$$\sum_{J=0}^M \mathbf{w}_J E_{\text{Hxc},J}^{\mathbf{w}}[n] = E_{\text{Hxc}}^{\mathbf{w}}[n]. \quad (17)$$

Eqs. (16) and (17), which are the second key result of this work, establish a clearer connection between ensemble and individual density-functional Hxc energies. Before analyzing the Hx and correlation terms separately for each state, it is worth noticing that, according to Eqs. (1), (5), and (6), the individual Hxc energies can also be expressed as follows:

$$\begin{aligned} E_{\text{Hxc},J}^{\mathbf{w}}[n^{\mathbf{w}}] &= E_{\text{Hxc}}^{\mathbf{w}}[n^{\mathbf{w}}] + \sum_{I=1}^M (\delta_{IJ} - \mathbf{w}_I) \\ &\times \left[ \frac{d}{d\mathbf{w}_I} \left( E_{\text{Hxc}}^{\mathbf{w}}[n^{\mathbf{w}}] \right) - \left. \frac{\partial E_{\text{Hxc}}^{\boldsymbol{\xi}}[n^{\boldsymbol{\xi},\mathbf{w}}]}{\partial \mathbf{w}_I} \right|_{\boldsymbol{\xi}=\mathbf{w}} \right], \end{aligned} \quad (18)$$

where the auxiliary double-weight ensemble KS density

$$n^{\boldsymbol{\xi},\mathbf{w}}(\mathbf{r}) = \sum_{K=0}^M \xi_K n_{\Phi_K^{\mathbf{w}}}(\mathbf{r}) \quad (19)$$

has been introduced. The term that is subtracted on the right-hand side of Eq. (18) originates from the fact that the ensemble energy is calculated variationally. It is in principle nonzero since the individual densities in the KS ensemble are weight-dependent, unlike in the true physical system.

*Exact individual Hartree-exchange energies.* Let us first focus on the individual Hx contributions to Eq. (18). As the dependence in  $\boldsymbol{\xi}$  of the double-weight ensemble density in Eq. (19) does not affect the individual KS densities, we conclude that  $\Phi_K^{\boldsymbol{\xi}}[n^{\boldsymbol{\xi},\mathbf{w}}] = \Phi_K^{\mathbf{w}}$ , thus leading to [see Eq. (3)],

$$E_{\text{Hx}}^{\boldsymbol{\xi}}[n^{\boldsymbol{\xi},\mathbf{w}}] = \sum_{K=0}^M \xi_K \langle \Phi_K^{\mathbf{w}} | \hat{W}_{\text{ee}} | \Phi_K^{\mathbf{w}} \rangle, \quad (20)$$

while  $E_{\text{Hx}}^{\mathbf{w}}[n^{\mathbf{w}}] = \sum_{K=0}^M \mathbf{w}_K \langle \Phi_K^{\mathbf{w}} | \hat{W}_{\text{ee}} | \Phi_K^{\mathbf{w}} \rangle$ . As a result, the individual Hx energy in Eq. (18) reduces to the simple and intuitive expression:

$$E_{\text{Hx},J}^{\mathbf{w}}[n^{\mathbf{w}}] = \langle \Phi_J^{\mathbf{w}} | \hat{W}_{\text{ee}} | \Phi_J^{\mathbf{w}} \rangle, \quad (21)$$

where, as emphasized previously,  $\Phi_J^{\mathbf{w}}$  can be a configuration state function [12].

*Density-driven correlation energies.* We now focus on the individual correlation energies with a particular emphasis on their SD/DD decomposition. We start from the density-functional expression of Eq. (16). Following Gould and Pittalis [31], we introduce the following correlation bifunctional of the ensemble and individual densities:

$$\begin{aligned} \mathcal{E}_{c,J}^{\mathbf{w}}[n, n_J] &= E_c^{\mathbf{w}}[n] + \sum_{I=1}^M (\delta_{IJ} - \mathbf{w}_I) \frac{\partial E_c^{\mathbf{w}}[n]}{\partial \mathbf{w}_I} \\ &+ \int d\mathbf{r} \frac{\delta E_c^{\mathbf{w}}[n]}{\delta n(\mathbf{r})} (n_{J}(\mathbf{r}) - n(\mathbf{r})). \end{aligned} \quad (22)$$

Note that the exact  $J$ th correlation energy is recovered by inserting the  $J$ th *noninteracting* KS density into the bifunctional:

$$E_{c,J}^{\mathbf{w}}[n^{\mathbf{w}}] = \mathcal{E}_{c,J}^{\mathbf{w}}[n^{\mathbf{w}}, n_{\Psi_J}]. \quad (23)$$

Note also that the bifunctional varies linearly with  $n_J$ . Interestingly, if we instead insert the true interacting density, a different correlation energy [that will be referred to as SD correlation energy in the following] will be obtained. Note that, according to Eq. (9), it can be expressed more explicitly as follows:

$$\begin{aligned} E_{c,J}^{\mathbf{w},\text{SD}}[n^{\mathbf{w}}] &:= \mathcal{E}_{c,J}^{\mathbf{w}}[n^{\mathbf{w}}, n_{\Psi_J}] \\ &= E_c^{\mathbf{w}}[n^{\mathbf{w}}] + \sum_{I=1}^M (\delta_{IJ} - \mathbf{w}_I) \frac{dE_c^{\mathbf{w}}[n^{\mathbf{w}}]}{d\mathbf{w}_I}, \end{aligned} \quad (24)$$

where, according to Eqs. (3), (5), and (6), the exact ensemble correlation energy reads

$$E_c^{\mathbf{w}}[n^{\mathbf{w}}] = \sum_{K=0}^M \mathbf{w}_K \left( \langle \hat{T} + \hat{W}_{\text{ee}} \rangle_{\Psi_K} - \langle \hat{T} + \hat{W}_{\text{ee}} \rangle_{\Phi_K^{\mathbf{w}}} \right). \quad (25)$$

The complementary DD correlation energy is then defined as

$$\begin{aligned} E_{c,J}^{\mathbf{w},\text{DD}}[n^{\mathbf{w}}] &:= E_{c,J}^{\mathbf{w}}[n^{\mathbf{w}}] - E_{c,J}^{\mathbf{w},\text{SD}}[n^{\mathbf{w}}] \\ &= \int d\mathbf{r} \frac{\delta E_c^{\mathbf{w}}[n^{\mathbf{w}}]}{\delta n(\mathbf{r})} (n_{\Phi_J^{\mathbf{w}}}(\mathbf{r}) - n_{\Psi_J}(\mathbf{r})). \end{aligned} \quad (26)$$

As readily seen from Eq. (26), the DD correlation energy vanishes for the ground state ( $J = 0$ ) when  $\mathbf{w} = \mathbf{0}$  since, in this case [which corresponds to regular DFT] the physical and KS ground states have exactly the same density. In addition, unlike in the original SD/DD decomposition of Gould and Pittalis [31], our DD correlation energies are *traceless*, i.e.

$$\sum_{J=0}^M \mathbf{w}_J E_{c,J}^{\mathbf{w},\text{DD}}[n^{\mathbf{w}}] = 0. \quad (27)$$

In other words, within our terminology, DD effects will contribute to individual correlation energies only, not to the ensemble one. One should stress that, even though the SD/DD correlation energy decomposition of Eq. (26) is very intuitive, as it is based on the idea that DD effects reflect differences in *density* between interacting and non-interacting wavefunctions, our formalism allows for other decompositions. For example, by rewriting our SD correlation energy more explicitly as follows [see Eqs. (24) and (25)]:

$$\begin{aligned} E_{c,J}^{\mathbf{w},\text{SD}}[n^{\mathbf{w}}] &= \langle \Psi_J | \hat{T} + \hat{W}_{\text{ee}} | \Psi_J \rangle - \langle \Phi_J^{\mathbf{w}} | \hat{T} + \hat{W}_{\text{ee}} | \Phi_J^{\mathbf{w}} \rangle \\ &- 2 \sum_{I=1}^M \sum_{K=0}^M (\delta_{IJ} - \mathbf{w}_I) \mathbf{w}_K \left\langle \Phi_K^{\mathbf{w}} \left| \hat{T} + \hat{W}_{\text{ee}} \right| \frac{\partial \Phi_K^{\mathbf{w}}}{\partial \mathbf{w}_I} \right\rangle, \end{aligned} \quad (28)$$

one may choose to remove in the summation over  $K$  all but the individual-state  $K = J$  contribution, thus making the decomposition more *wavefunction*-based. This leads to an alternative definition for the SD correlation energy,

$$\begin{aligned} \overline{E}_{c,J}^{\mathbf{w},\text{SD}}[n^{\mathbf{w}}] &= \langle \Psi_J | \hat{T} + \hat{W}_{\text{ee}} | \Psi_J \rangle - \langle \Phi_J^{\mathbf{w}} | \hat{T} + \hat{W}_{\text{ee}} | \Phi_J^{\mathbf{w}} \rangle \\ &- 2 \sum_{I=1}^M (\delta_{IJ} - \mathbf{w}_I) \mathbf{w}_J \left\langle \Phi_J^{\mathbf{w}} \left| \hat{T} + \hat{W}_{\text{ee}} \right| \frac{\partial \Phi_J^{\mathbf{w}}}{\partial \mathbf{w}_I} \right\rangle, \end{aligned} \quad (29)$$

which can be connected to the one proposed by Gould and Pittalis [31]. Indeed, if the state-specific KS wavefunction the authors referred to is replaced by the more explicit expression  $\Phi_J^{\mathbf{w}} + \mathbf{w}_J \sum_{I=1}^M (\delta_{IJ} - \mathbf{w}_I) \partial \Phi_J^{\mathbf{w}} / \partial \mathbf{w}_I$ , we recover Eq. (29) through first order in  $\mathbf{w}_J$ . In this case, the complementary DD correlation energy will of course differ from the one in Eq. (26) but both decompositions should return the same individual correlation energy  $\overline{E}_{c,J}^{\mathbf{w},\text{SD}}[n^{\mathbf{w}}] + \overline{E}_{c,J}^{\mathbf{w},\text{DD}}[n^{\mathbf{w}}] = E_{c,J}^{\mathbf{w},\text{SD}}[n^{\mathbf{w}}] + E_{c,J}^{\mathbf{w},\text{DD}}[n^{\mathbf{w}}]$ . It is worth noticing that the DD correlation energies will not be traceless anymore,

$$\begin{aligned} \sum_{J=0}^M \mathbf{w}_J \overline{E}_{c,J}^{\mathbf{w},\text{DD}}[n^{\mathbf{w}}] &= 2 \sum_{J=0}^M \mathbf{w}_J^2 \sum_{I=1}^M (\delta_{IJ} - \mathbf{w}_I) \\ &\times \left\langle \Phi_J^{\mathbf{w}} \left| \hat{T} + \hat{W}_{\text{ee}} \right| \frac{\partial \Phi_J^{\mathbf{w}}}{\partial \mathbf{w}_I} \right\rangle \neq 0, \end{aligned} \quad (30)$$

as expected from Ref. [31]. In the rest of this work we will continue exploring the decomposition of Eq. (26).

In a practical calculation, one would use the following equivalent expression [see Eq. (10)] in order to evaluate each DD correlation energy individually:

$$\begin{aligned} E_{c,J}^{\mathbf{w},\text{DD}}[n^{\mathbf{w}}] &= - \sum_{I=1}^M \sum_{K=0}^M (\delta_{IJ} - \mathbf{w}_I) \mathbf{w}_K \\ &\times \int d\mathbf{r} \frac{\delta E_c^{\mathbf{w}}[n^{\mathbf{w}}]}{\delta n(\mathbf{r})} \frac{\partial n_{\Phi_K^{\mathbf{w}}}(\mathbf{r})}{\partial \mathbf{w}_I}, \end{aligned} \quad (31)$$

or, in a more compact way [see Eq. (19)],

$$E_{c,J}^{\mathbf{w},\text{DD}}[n^{\mathbf{w}}] = - \sum_{I=1}^M (\delta_{IJ} - \mathbf{w}_I) \left. \frac{\partial E_c^{\xi}[n^{\xi,\mathbf{w}}]}{\partial \mathbf{w}_I} \right|_{\xi=\mathbf{w}}, \quad (32)$$

where the derivatives in  $\mathbf{w}$  of the KS densities would be obtained by solving our central linear response Eq. (13). In the light of Eq. (18) and the comment that follows Eq. (19), we conclude from Eqs. (24) and (32) that neglecting DD correlations is analogous to ignoring the variational character of the ensemble energy when extracting (by differentiation) individual correlation energies from the latter.

*Application.* Gould and Pittalis [31] have shown that DD effects can contribute substantially to correlation energies. We will show that, even though we use a different SD/DD decomposition, we reach exactly the same conclusion. For that purpose, we consider the two-electron Hubbard dimer model [14–17, 24, 37] that can be seen as a prototype for a diatomic molecule. In this simple but nontrivial model, the density  $n$  reduces to a (possibly fractional) number that corresponds to the occupation of the first atomic site [the occupation of the second atom is then  $2 - n$ ]. It is governed by three parameters: the hopping  $t$  that modulates the strength of the kinetic energy, the on-site two-electron repulsion strength  $U$ , and the external potential difference  $\Delta v_{\text{ext}}$  which controls the asymmetry in the dimer. For simplicity, we focus on the weakly asymmetric and strongly correlated regime  $\Delta v_{\text{ext}}/t \ll t/U \ll 1$ . In this case, the ground state remains essentially symmetric [14], i.e.  $n_{\Psi_0} \approx 1$ , and the density of the first (singlet) excited state [whose charge-transfer character increases with  $\Delta v_{\text{ext}}/t$ ] varies through first order in  $\Delta v_{\text{ext}}/t$  as  $n_{\Psi_1} \approx 1 + [(U\Delta v_{\text{ext}})/(2t^2)]$  [15]. As a result, the bi-ensemble density reads

$$n^{\mathbf{w}} \approx 1 + \frac{\mathbf{w}U\Delta v_{\text{ext}}}{2t^2}, \quad (33)$$

where  $\mathbf{w} \equiv \mathbf{w}_1$ . As mentioned in the introduction, the KS excited state is always symmetric ( $n_{\Phi_1^{\mathbf{w}}} = 1$ ), even when the true interacting system is not. Therefore, the KS ground-state density equals  $n_{\Phi_0^{\mathbf{w}}} = (n^{\mathbf{w}} - \mathbf{w})/(1 - \mathbf{w})$ , thus leading to

$$n_{\Phi_0^{\mathbf{w}}} \approx 1 + \frac{\mathbf{w}U\Delta v_{\text{ext}}}{2t^2(1 - \mathbf{w})}. \quad (34)$$

As shown in Ref. [15], in the strongly correlated regime, the ensemble correlation functional reads, for  $|n - 1| \leq \mathbf{w}$ , as follows:

$$E_c^{\mathbf{w}}(n) \approx -\frac{U}{2} \left[ (1 - \mathbf{w}) - \frac{(3\mathbf{w} - 1)(n - 1)^2}{(1 - \mathbf{w})^2} \right]. \quad (35)$$

Individual SD/DD correlation energies can then be obtained from Eqs. (24) and (32), thus leading to the final expressions:

$$E_{c,J=0}^{\mathbf{w},\text{SD}}(n^{\mathbf{w}}) \approx -\frac{U}{2} + \frac{U(U\Delta v_{\text{ext}})^2 \mathbf{w}^2(1 - 5\mathbf{w})}{8t^4(1 - \mathbf{w})^3},$$

$$E_{c,J=0}^{\mathbf{w},\text{DD}}(n^{\mathbf{w}}) \approx \frac{U(U\Delta v_{\text{ext}})^2 \mathbf{w}^2(3\mathbf{w} - 1)}{4t^4(1 - \mathbf{w})^3}, \quad (36)$$

for the ground state, and

$$E_{c,J=1}^{\mathbf{w},\text{SD}}(n^{\mathbf{w}}) \approx \frac{U(U\Delta v_{\text{ext}})^2 \mathbf{w}(4\mathbf{w} - 1)}{4t^4(1 - \mathbf{w})^2},$$

$$E_{c,J=1}^{\mathbf{w},\text{DD}}(n^{\mathbf{w}}) \approx \frac{U(U\Delta v_{\text{ext}})^2 \mathbf{w}(1 - 3\mathbf{w})}{4t^4(1 - \mathbf{w})^2}, \quad (37)$$

for the excited state. As pointed out in Ref. [31] and readily seen from Eq. (36), when  $\mathbf{w} > 1/3$ , DD correlation energies can be positive. In the excited state, our SD correlation energy is also positive when  $\mathbf{w} > 1/4$  [see Eq. (37)]. This is not surprising as the energy extraction procedure used in Eq. (15) is *not* variational, even though the ensemble energy is. Interestingly, in the excited state, the DD/SD correlation energy ratio is  $|(3\mathbf{w} - 1)/(4\mathbf{w} - 1)|$ , which gives 50% for an equiensemble ( $\mathbf{w} = 1/2$ ), thus illustrating the importance of DD effects, at least in the considered (strongly correlated) regime.

*Summary and outlook.* Exact expressions for individual correlation energies within a density-functional ensemble, as well as their subsequent state-driven (SD)/density-driven (DD) decomposition, have been derived. Unlike Gould and Pittalis [31], we did not have to refer to additional state-specific KS systems. By uncovering the individual components of ensemble correlation energies we make a crucial step toward the development of first-principle density functionals for ensembles. While we focused on the extraction of individual properties, extensions to the calculation of couplings between states should be explored. Work is currently in progress in these directions.

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