Individual Correlations in Ensemble Density Functional Theory: State- and Density-Driven Decompositions without Additional Kohn-Sham Systems

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Gould and Pittalis [Phys. Rev. Lett. **123**, 016401 (2019) recently revealed a density-driven (DD) correlation energy that is specific to many-electron ensembles and must be accounted for by approximations. We derive in this Letter a general and simpler expression in terms of the ensemble weights, the ensemble Kohn-Sham (KS) orbitals, and their linear response to variations in the ensemble weights. As no additional state-driven KS systems are needed, its evaluation is greatly simplified. We confirm the importance of DD effects and introduce a direct and promising route to approximations.

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Introduction.—Time-dependent density functional theory (TDDFT) [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, TDDFT 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 [3–25].

Gross-Oliveira-Kohn (GOK) ensemble DFT [26–28], which is a generalization of Theophilou's DFT for equi-ensembles [29,30], is one of these (low-cost) alternatives. Unlike state-averaged quantum chemical methods [31], GOKDFT describes (in principle exactly) each state that belongs 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 GOKDFT, the noninteracting 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 [32,33], is central in the Gould-Pittalis correlation energy decomposition into state-driven (SD) and density-driven (DD) contributions [32].

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 [12,18,25,34]. The way such a decomposition should be written and implemented is, however, open to discussion. Gould and Pittalis [32] 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. For real *ab initio* (and therefore Coulombic) systems, a unique KS system can indeed be designed from a given excited-state density by requiring, as an additional constraint, the KS ground-state density to be as close as possible to the ground-state Coulomb one, as shown by Ayers *et al.* [35–37]. If model systems are considered instead (in order to minimize numerical efforts), one may then face nonuniqueness or representability issues when constructing a KS potential for each excited state within the ensemble. The nonuniqueness problem can be solved through a selection procedure [32]. But there might also be situations where such a potential does not exist. A simple example is given by the two-electron asymmetric Hubbard dimer [38] where the occupation of the atomic sites plays the role of the density. In the noninteracting 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 [15].

As shown in this Letter, the nonuniqueness or nonexistence 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) [27], simply because individual-state properties can be extracted in principle exactly from the KS density functional ensemble. An exact expression for the individual density functional correlation energies is derived and, on that basis, two different SD-DD decompositions are explored. While being simpler and more general (i.e., applicable to all systems) than the Gould-Pittalis decomposition [32], one of them offers a clearer way to model ensemble correlation energies.

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A brief review of GOKDFT.—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 $\hat{H} = \hat{T} + \hat{W}_{\mathrm{ee}} + \hat{V}_{\mathrm{ext}}$ is the sum of the N-electron kinetic energy, Coulomb repulsion, and local multiplicative external potential $\hat{V}_{\mathrm{ext}} \equiv \sum_{i=1}^{N} v_{\mathrm{ext}}(\mathbf{r}_i)\times$ operators, respectively. For simplicity, we will assume that the energies are not degenerate, i.e., $E_0 < E_1 < \cdots < E_M$. Note that the theory can be easily extended to multiplets by assigning the same ensemble weight to degenerate states [27]. The ensemble energy $E^{\mathbf{w}} = \sum_{I=0}^{M} \mathsf{w}_I E_I$ 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., $\mathsf{w}_0 = 1 - \sum_{I=1}^{M} \mathsf{w}_I$, so that only the weights assigned to the excited states $\mathbf{w} \equiv (\mathsf{w}_1, \mathsf{w}_2, \ldots, \mathsf{w}_M)$ are allowed to vary independently.

In GOKDFT, the ensemble energy is determined as follows for given and fixed weights $\mathbf{w}$ [27]:

$$E^{\mathbf{w}} = \min_{\{\varphi_k\}} \{\mathrm{Tr}[\hat{\gamma}^{\mathbf{w}}(\hat{T} + \hat{V}_{\mathrm{ext}})] + E^{\mathbf{w}}_{Hxc}[n_{\hat{\gamma}^{\mathbf{w}}}]\}, \tag{1}$$

where Tr denotes the trace, $\hat{\gamma}^{\mathbf{w}} = \sum_{I=0}^{M} \mathsf{w}_I |\Phi_I\rangle\langle\Phi_I|$, and $n_{\hat{\gamma}^{\mathbf{w}}}(\mathbf{r}) = \sum_{I=0}^{M} \mathsf{w}_I n_{\Phi_I}(\mathbf{r})$ is a trial ensemble density. The trial determinants (or configuration state functions) Φ_I are all generated from the same set $\{\varphi_k\}$ of orthonormal molecular orbitals that are optimized variationally. The ensemble Hartree-exchange-correlation (Hxc) density functional in Eq. (1) can be decomposed exactly as $E^{\mathbf{w}}_{Hxc}[n] = E^{\mathbf{w}}_{Hx}[n] + E^{\mathbf{w}}_{c}[n]$, where the ensemble density functional Hx energy [13]

$$E^{\mathbf{w}}_{Hx}[n] = \sum_{K=0}^{M} \mathsf{w}_K \langle \Phi^{\mathbf{w}}_K[n] | \hat{W}_{\mathrm{ee}} | \Phi^{\mathbf{w}}_K[n] \rangle \tag{2}$$

is evaluated from the KS ensemble that reproduces the density n:

$$\sum_{K=0}^{M} \mathsf{w}_K n_{\Phi^{\mathbf{w}}_K[n]}(\mathbf{r}) = n(\mathbf{r}). \tag{3}$$

Note that, in the general case, the N-electron KS wave functions $\{\Phi^{\mathbf{w}}_K[n]\}_{0\leq K\leq M}$ can be configuration state functions [13], 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 [7,15]. The minimizing KS wave functions $\{\Phi^{\mathbf{w}}_I = \Phi^{\mathbf{w}}_I[n^{\mathbf{w}}]\}_{0\leq I\leq M}$ in Eq. (1) reproduce the exact ensemble density $n^{\mathbf{w}}$:

$$\sum_{I=0}^{M} \mathsf{w}_I n_{\Phi^{\mathbf{w}}_I}(\mathbf{r}) = \sum_{I=0}^{M} \mathsf{w}_I n_{\Psi_I}(\mathbf{r}) = n^{\mathbf{w}}(\mathbf{r}), \tag{4}$$

so that the exact ensemble energy can be expressed as

$$E^{\mathbf{w}} = \sum_{I=0}^{M} \mathsf{w}_I \langle \Phi^{\mathbf{w}}_I | \hat{T} + \hat{V}_{\mathrm{ext}} | \Phi^{\mathbf{w}}_I \rangle + E^{\mathbf{w}}_{Hxc}[n^{\mathbf{w}}]. \tag{5}$$

The corresponding minimizing orbitals fulfill the ensemble KS equations [27],

$$\left[-\frac{\nabla^2}{2} + v_{\mathrm{ext}}(\mathbf{r}) + v^{\mathbf{w}}_{Hxc}[n^{\mathbf{w}}](\mathbf{r})\right]\varphi^{\mathbf{w}}_p(\mathbf{r}) = \varepsilon^{\mathbf{w}}_p \varphi^{\mathbf{w}}_p(\mathbf{r}), \tag{6}$$

where $v^{\mathbf{w}}_{Hxc}[n](\mathbf{r}) = \delta E^{\mathbf{w}}_{Hxc}[n]/\delta n(\mathbf{r})$ is the ensemble Hxc density functional potential. When the KS wave functions are single determinants, their density simply reads

$$n_{\Phi^{\mathbf{w}}_I}(\mathbf{r}) = \sum_p \theta^I_p |\varphi^{\mathbf{w}}_p(\mathbf{r})|^2, \tag{7}$$

where θ^I_p is the (fixed and integer) occupation number of the orbital $\varphi^{\mathbf{w}}_p$ in the determinant $\Phi^{\mathbf{w}}_I$.

Extracting exact individual densities.—As pointed out in Ref. [32], Eq. (4) does not imply that the KS wave functions 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 [25], the density of any (ground or excited) state can be extracted from the (linear-in-$\mathbf{w}$) ensemble density as follows:

$$n_{\Psi_J}(\mathbf{r}) = n^{\mathbf{w}}(\mathbf{r}) + \sum_{I=1}^{M} (\delta_{IJ} - \mathsf{w}_I) \frac{\partial n^{\mathbf{w}}(\mathbf{r})}{\partial \mathsf{w}_I}. \tag{8}$$

By inserting the KS ensemble density expression of Eq. (4) into Eq. (8) we obtain our first key result, namely, the exact deviation in density of the true interacting state from the KS one,

$$n_{\Psi_J}(\mathbf{r}) - n_{\Phi^{\mathbf{w}}_J}(\mathbf{r}) = \sum_{I=1}^{M} \sum_{K=0}^{M} (\delta_{IJ} - \mathsf{w}_I)\mathsf{w}_K \frac{\partial n_{\Phi^{\mathbf{w}}_K}(\mathbf{r})}{\partial \mathsf{w}_I}, \tag{9}$$

where $\partial n_{\Phi^{\mathbf{w}}_K}(\mathbf{r})/\partial \mathsf{w}_I = 2\sum_p \theta^K_p \varphi^{\mathbf{w}}_p(\mathbf{r}) \partial\varphi^{\mathbf{w}}_p(\mathbf{r})/\partial \mathsf{w}_I$. As readily seen, the (static) linear response of the KS orbitals to variations in the ensemble weights becomes central. In practice, it may be evaluated by finite differences. A numerically more robust approach, which requires additional implementation work, would consist in solving an ensemble coupled-perturbed equation which is derived in the Supplemental Material [39], by analogy with Ref. [40].

Individual Hxc energies.—The next step consists in extracting individual Hxc density functional energies from the KS ensemble. For that purpose, we use the analog of

Eq. (8) for energies [25] which, when combined with the variational KS expression of the ensemble energy in Eqs. (1) and (5), leads to the following exact energy level expression:

$$E_J = \langle \Phi^{\mathbf{w}}_J | \hat{T} + \hat{V}_{\mathrm{ext}} | \Phi^{\mathbf{w}}_J \rangle + E^{\mathbf{w}}_{Hxc,J}[n^{\mathbf{w}}], \tag{10}$$

where the individual density functional Hxc energy reads

$$E^{\mathbf{w}}_{Hxc,J}[n] = E^{\mathbf{w}}_{Hxc}[n] + \sum_{I=1}^{M} (\delta_{IJ} - \mathsf{w}_I) \frac{\partial E^{\mathbf{w}}_{Hxc}[n]}{\partial \mathsf{w}_I} + \int d\mathbf{r} \frac{\delta E^{\mathbf{w}}_{Hxc}[n]}{\delta n(\mathbf{r})} (n_{\Phi^{\mathbf{w}}_J[n]}(\mathbf{r}) - n(\mathbf{r})). \tag{11}$$

Note that, as expected, the ensemble density functional Hxc energy is recovered from the weighted sum of the individual Hxc energies [see Eqs. (3) and (11)]:

$$\sum_{J=0}^{M} \mathsf{w}_J E^{\mathbf{w}}_{Hxc,J}[n] = E^{\mathbf{w}}_{Hxc}[n]. \tag{12}$$

Equations (11) and (12) 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), (4), and (5), the individual Hxc energy can be rewritten as follows:

$$E^{\mathbf{w}}_{Hxc,J}[n^{\mathbf{w}}] = E^{\mathbf{w}}_{Hxc}[n^{\mathbf{w}}] + \sum_{I=1}^{M} (\delta_{IJ} - \mathsf{w}_I) \times \left[\frac{\partial}{\partial \mathsf{w}_I} (E^{\mathbf{w}}_{Hxc}[n^{\mathbf{w}}]) - \left. \frac{\partial E^{\boldsymbol{\xi}}_{Hxc}[n^{\boldsymbol{\xi},\mathbf{w}}]}{\partial \mathsf{w}_I} \right|_{\boldsymbol{\xi}=\mathbf{w}} \right], \tag{13}$$

where the auxiliary double-weight ensemble KS density

$$n^{\boldsymbol{\xi},\mathbf{w}}(\mathbf{r}) = \sum_{K=0}^{M} \xi_K n_{\Phi^{\mathbf{w}}_K}(\mathbf{r}) \tag{14}$$

has been introduced. The term that is subtracted on the right-hand side of Eq. (13) 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. (13). As the dependence in $\boldsymbol{\xi}$ of the double-weight ensemble density in Eq. (14) does not affect the individual KS densities, we conclude that $\Phi^{\boldsymbol{\xi}}_K[n^{\boldsymbol{\xi},\mathbf{w}}] = \Phi^{\mathbf{w}}_K$, thus leading to [see Eq. (2)]

$$E^{\boldsymbol{\xi}}_{Hx}[n^{\boldsymbol{\xi},\mathbf{w}}] = \sum_{K=0}^{M} \xi_K \langle \Phi^{\mathbf{w}}_K | \hat{W}_{\mathrm{ee}} | \Phi^{\mathbf{w}}_K \rangle, \tag{15}$$

while $E^{\mathbf{w}}_{Hx}[n^{\mathbf{w}}] = \sum_{K=0}^{M} \mathsf{w}_K \langle \Phi^{\mathbf{w}}_K | \hat{W}_{\mathrm{ee}} | \Phi^{\mathbf{w}}_K \rangle$. As a result, the individual Hx energy in Eq. (13) reduces to the simple and intuitive expression

$$E^{\mathbf{w}}_{Hx,J}[n^{\mathbf{w}}] = \langle \Phi^{\mathbf{w}}_J | \hat{W}_{\mathrm{ee}} | \Phi^{\mathbf{w}}_J \rangle, \tag{16}$$

where, as emphasized previously, $\Phi^{\mathbf{w}}_J$ can be a configuration state function [13].

State- and density-driven correlations.—We now focus on the individual correlation energies and their subsequent SD-DD decomposition. We start from the decomposition into individual components of the ensemble density functional correlation energy [32],

$$E^{\mathbf{w}}_{\mathrm{c}}[n] = \sum_{K=0}^{M} \mathsf{w}_K \mathcal{E}^{\mathbf{w}}_{\mathrm{c},K}[n], \tag{17}$$

where $\mathcal{E}^{\mathbf{w}}_{\mathrm{c},K}[n^{\mathbf{w}}] = \langle \Psi_K | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi_K \rangle - f^{\mathbf{w}}_K[n^{\mathbf{w}}]$ and $f^{\mathbf{w}}_K[n^{\mathbf{w}}] = \langle \Phi^{\mathbf{w}}_K | \hat{T} + \hat{W}_{\mathrm{ee}} | \Phi^{\mathbf{w}}_K \rangle$ is the Kth component of the exchange-only GOK functional $f^{\mathbf{w}}[n] \coloneqq \sum_{K=0}^{M} \mathsf{w}_K f^{\mathbf{w}}_K[n]$. By inserting Eq. (17) into Eq. (13) and using Eq. (9) we obtain the following exact expression for the individual correlation energy within the ensemble:

$$E^{\mathbf{w}}_{\mathrm{c},J}[n^{\mathbf{w}}] = \mathcal{E}^{\mathbf{w}}_{\mathrm{c},J}[n^{\mathbf{w}}] + \sum_{K=0}^{M} \mathsf{w}_K \sum_{I=1}^{M} (\delta_{IJ} - \mathsf{w}_I) \frac{\partial}{\partial \mathsf{w}_I} (\mathcal{E}^{\mathbf{w}}_{\mathrm{c},K}[n^{\mathbf{w}}]) + \sum_{K=0}^{M} \mathsf{w}_K \int d\mathbf{r} \frac{\delta \mathcal{E}^{\mathbf{w}}_{\mathrm{c},K}[n^{\mathbf{w}}]}{\delta n(\mathbf{r})} (n_{\Phi^{\mathbf{w}}_J}(\mathbf{r}) - n_{\Psi_J}(\mathbf{r})), \tag{18}$$

which, as readily seen, is *not* equal to the Jth component $\mathcal{E}^{\mathbf{w}}_{\mathrm{c},J}[n^{\mathbf{w}}]$ of the ensemble correlation energy. This is a major difference between exchange and correlation energies in ensembles. As shown in the Supplemental Material [39], it originates from the fact that individual correlation energies incorporate the density correction that must be applied to each KS state in order to recover the exact individual external potential energies.

Interestingly, a first SD-DD decomposition, that we may refer to as *density* based, naturally emerges from Eq. (18). Indeed, substituting the true individual densities for the KS ones leaves the first two terms on the right-hand side unchanged (as the KS and true ensemble densities match) while the last term vanishes. Thus we may define individual SD correlation energies as follows:

$$E^{\mathbf{w},\mathrm{SD}}_{\mathrm{c},J}[n^{\mathbf{w}}] \coloneqq \mathcal{E}^{\mathbf{w}}_{\mathrm{c},J}[n^{\mathbf{w}}] + \sum_{K=0}^{M} \mathsf{w}_K \sum_{I=1}^{M} (\delta_{IJ} - \mathsf{w}_I) \frac{\partial}{\partial \mathsf{w}_I} (\mathcal{E}^{\mathbf{w}}_{\mathrm{c},K}[n^{\mathbf{w}}]), \tag{19}$$

or, equivalently, $E^{\mathbf{w},\mathrm{SD}}_{\mathrm{c},J}[n^{\mathbf{w}}] = E^{\mathbf{w}}_{\mathrm{c}}[n^{\mathbf{w}}] + \sum_{I=1}^{M} (\delta_{IJ} - \mathsf{w}_I) \times (\partial/\partial \mathsf{w}_I)(E^{\mathbf{w}}_{\mathrm{c}}[n^{\mathbf{w}}])$. As readily seen from Eq. (13), the complementary DD contribution [third term on the right-hand side of Eq. (18)] will then be defined as

$$E^{\mathbf{w},\mathrm{DD}}_{\mathrm{c},J}[n^{\mathbf{w}}] := -\sum_{I=1}^{M}(\delta_{IJ}-\mathsf{w}_I)\left.\frac{\partial E_{\mathrm{c}}^{\boldsymbol{\xi}}[n^{\boldsymbol{\xi},\mathbf{w}}]}{\partial \mathsf{w}_I}\right|_{\boldsymbol{\xi}=\mathbf{w}}. \quad (20)$$

Such a decomposition is of course arbitrary and not unique. One may opt for a more *state*-based approach where only the terms in Eq. (19) that originate from the individual state J are included into the state-driven part of the correlation energy, thus leading to a second definition (that we denote $\overline{\mathrm{SD}}$ to distinguish the two decompositions):

$$E^{\mathbf{w},\overline{\mathrm{SD}}}_{\mathrm{c},J}[n^{\mathbf{w}}] := \mathcal{E}^{\mathbf{w}}_{\mathrm{c},J}[n^{\mathbf{w}}] + \mathsf{w}_J\sum_{I=1}^{M}(\delta_{IJ}-\mathsf{w}_I)\frac{\partial}{\partial \mathsf{w}_I}(\mathcal{E}^{\mathbf{w}}_{\mathrm{c},J}[n^{\mathbf{w}}]), \quad (21)$$

which may be rewritten as [39]

$$E^{\mathbf{w},\overline{\mathrm{SD}}}_{\mathrm{c},J}[n^{\mathbf{w}}] = \langle\Psi_J|\hat{T}+\hat{W}_{\mathrm{ee}}|\Psi_J\rangle - \bar{f}^{\mathbf{w}}_J[n^{\mathbf{w}}], \quad (22)$$

where the *effective* individual exchange-only GOK energy reads

$$\bar{f}^{\mathbf{w}}_J[n^{\mathbf{w}}] = f^{\mathbf{w}}_J[n^{\mathbf{w}}] + \mathsf{w}_J\sum_{I=1}^{M}(\delta_{IJ}-\mathsf{w}_I)\frac{\partial f^{\mathbf{w}}_J[n^{\mathbf{w}}]}{\partial \mathsf{w}_I}, \quad (23)$$

and the Jth component of the exchange-only density functional GOK energy can be extracted from the ensemble one as follows:

$$f^{\mathbf{w}}_J[n^{\mathbf{w}}] = f^{\mathbf{w}}[n^{\mathbf{w}}] + \sum_{I=1}^{M}(\delta_{IJ}-\mathsf{w}_I)\left.\frac{\partial f^{\boldsymbol{\xi}}[n^{\boldsymbol{\xi},\mathbf{w}}]}{\partial \xi_I}\right|_{\boldsymbol{\xi}=\mathbf{w}}. \quad (24)$$

Equations (22)–(24) are the second key result of this Letter. They clearly show that a Gould-Pittalis–like [32] state-driven correlation energy can be constructed without any additional state-specific KS system. The latter is somehow implicitly defined in the present approach through the extraction procedure described in Eqs. (23) and (24), thus circumventing potential representability and nonuniqueness issues mentioned in the introduction. Note that the first (SD) and second ($\overline{\mathrm{SD}}$) correlation energies can be connected as follows:

$$E^{\mathbf{w},\overline{\mathrm{SD}}}_{\mathrm{c},J}[n^{\mathbf{w}}] = E^{\mathbf{w},\mathrm{SD}}_{\mathrm{c},J}[n^{\mathbf{w}}] + \sum_{K\neq J}^{M}\sum_{I=1}^{M}\mathsf{w}_K(\delta_{IJ}-\mathsf{w}_I)\frac{\partial f^{\mathbf{w}}_K[n^{\mathbf{w}}]}{\partial \mathsf{w}_I}. \quad (25)$$

Moreover, as both decompositions should return the same individual correlation energy, the complementary $\overline{\mathrm{DD}}$ part will simply be defined as $E^{\mathbf{w},\overline{\mathrm{DD}}}_{\mathrm{c},J}[n^{\mathbf{w}}] := E^{\mathbf{w},\mathrm{DD}}_{\mathrm{c},J}[n^{\mathbf{w}}] - (E^{\mathbf{w},\overline{\mathrm{SD}}}_{\mathrm{c},J}[n^{\mathbf{w}}] - E^{\mathbf{w},\mathrm{SD}}_{\mathrm{c},J}[n^{\mathbf{w}}])$.

Let us now discuss the relevance of the two (in-principle-exact) decompositions. Opting for one or the other will depend, in practical calculations, on the level of approximation that is considered. If one is able to construct a functional that incorporates weight dependencies (from a finite uniform electron gas [41], for example), then the first decomposition can be applied straightforwardly in order to compute the energy levels (and properties) of the excited states. In the most common situation, where no weight-dependent functional is available, the second decomposition might be preferred. One of the reasons is that individual DD correlation energies [see Eq. (20)] read $\sum_{I=1}^{M}(\delta_{IJ}-\mathsf{w}_I)\Delta_I$ and, since $\sum_{J=0}^{M}\sum_{I=1}^{M}\mathsf{w}_J(\delta_{IJ}-\mathsf{w}_I)\Delta_I = 0$, they are traceless, i.e.,

$$\sum_{J=0}^{M}\mathsf{w}_J E^{\mathbf{w},\mathrm{DD}}_{\mathrm{c},J}[n^{\mathbf{w}}] = 0. \quad (26)$$

In other words, DD correlations contribute to the individual energies, not to the ensemble one. This statement holds at any level of approximation, by construction. As a result, the (first) SD-DD decomposition cannot be used for developing density functional approximations to the ensemble correlation energy. As further discussed in the following, the (second) $\overline{\mathrm{SD}}$-$\overline{\mathrm{DD}}$ decomposition is more appealing in this respect, simply because $\overline{\mathrm{DD}}$ correlations are *not* traceless. As shown in the Supplementary Material [39], the total $\overline{\mathrm{DD}}$ ensemble correlation energy can be evaluated exactly from the linear response of the exchange-only GOK energy components as follows:

$$E^{\mathbf{w},\overline{\mathrm{DD}}}_{\mathrm{c}}[n^{\mathbf{w}}] = \sum_{J=0}^{M}\mathsf{w}_J^2\sum_{I=1}^{M}(\delta_{IJ}-\mathsf{w}_I)\frac{\partial f^{\mathbf{w}}_J[n^{\mathbf{w}}]}{\partial \mathsf{w}_I}. \quad (27)$$

Approximations.—The most challenging task in GOKDFT, namely, the design of correlation density functionals for ensembles, can now be addressed by modeling $\overline{\mathrm{SD}}$ and $\overline{\mathrm{DD}}$ ensemble correlations separately. For the former, one may rely on the conventional ground-state limit of GOKDFT, i.e., $E^{\mathbf{w},\overline{\mathrm{SD}}}_{\mathrm{c},J}[n^{\mathbf{w}}] \approx E^{\mathbf{w}=\mathbf{0},\overline{\mathrm{SD}}}_{\mathrm{c},J}[n_{\Psi_0}]$, where, according to Eqs. (22) and (23), $E^{\mathbf{w}=\mathbf{0},\overline{\mathrm{SD}}}_{\mathrm{c},J=0}[n_{\Psi_0}] = E_{\mathrm{c}}[n_{\Psi_0}]$ is the conventional ground-state density functional correlation energy and $E^{\mathbf{w}=\mathbf{0},\overline{\mathrm{SD}}}_{\mathrm{c},J}[n_{\Psi_0}] \overset{J>0}{=} \langle\Psi_J|\hat{T}+\hat{W}_{\mathrm{ee}}|\Psi_J\rangle - \langle\Phi_J|\hat{T}+\hat{W}_{\mathrm{ee}}|\Phi_J\rangle$, Φ_J being an excited KS wave function based on a regular DFT calculation. Starting from the crudest ground-state-correlation only (GSC$\overline{\mathrm{SD}}$) weight-dependent approximation, $E^{\mathbf{w},\overline{\mathrm{SD}}}_{\mathrm{c}}[n^{\mathbf{w}}] \overset{\mathrm{GSC}\overline{\mathrm{SD}}}{\approx} (1-\sum_{J=1}^{M}\mathsf{w}_J)E_{\mathrm{c}}[n_{\Psi_0}]$, correlation in the excited states might be introduced in various ways, as explored in a recent work by Gould and Pittalis [33]. One may also learn either from models such as finite electron gases [41] or even from TDDFT excitation energies ω_J through the following exact relation:

$$E_{c,J}^{\mathbf{w}=\mathbf{0},\overline{SD}}[n_{\Psi_0}] \overset{J>0}{=} E_0 + \omega_J - \langle \Phi_J|\hat{H}|\Phi_J\rangle - \int d\mathbf{r} v_{\text{ext}}(\mathbf{r})(n_{\Psi_J}(\mathbf{r}) - n_{\Phi_J}(\mathbf{r})), \quad (28)$$

and Eq. (9), for the evaluation of the density difference. As GSC$\overline{\text{SD}}$ turned out to be accurate enough for the Hubbard dimer (see the next section), we leave the design of approximations beyond GSC$\overline{\text{SD}}$ for future work. On the other hand, the $\overline{\text{DD}}$ part in Eq. (27) can be evaluated accurately through finite differences with optimized effective potential techniques [12]. We propose here a simpler ground-state-exchange functional approximation (GSX$\overline{\text{DD}}$), $f^{\xi}[n^{\xi,\mathbf{w}}] \overset{\text{GSX}\overline{\text{DD}}}{\approx} \sum_{K=0}^{M} \xi_K \langle \Phi_K^{\mathbf{w}}|\hat{T}|\Phi_K^{\mathbf{w}}\rangle + E_{Hx}[n^{\xi,\mathbf{w}}]$, which is tested in the following.

Application.—We will now explore the two decompositions in the asymmetric two-electron Hubbard dimer model [15–18,25,38] where, due to representability issues mentioned previously, the Gould-Pittalis decomposition cannot be applied. The Hubbard dimer can be seen as a prototype for a diatomic molecule where 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 Δv_{ext} which controls the asymmetry of 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 singlet biensemble density reads [15,16,39] $n^{\mathsf{w}} \approx 1 + \mathsf{w}\eta$, where $\mathsf{w} \equiv \mathsf{w}_1$ and $\eta = (U\Delta v_{\text{ext}})/(2t^2) \ll 1$. As shown in the Supplemental Material [39], each individual correlation energy (and the subsequent decompositions) can be derived analytically. For example, for the excited state (whose charge-transfer character increases with $\Delta v_{\text{ext}}/t$), we obtain the following expressions [we denote $\mathcal{E} \equiv E/(U\eta^2)$ energies per unit of $U\eta^2$]:

$$\mathcal{E}_{c,J=1}^{\mathsf{w},\text{SD}}(n^{\mathsf{w}}) \approx \frac{\mathsf{w}(4\mathsf{w}-1)}{(1-\mathsf{w})^2}, \mathcal{E}_{c,J=1}^{\mathsf{w},\overline{\text{SD}}}(n^{\mathsf{w}}) \approx \frac{3\mathsf{w}^2}{(1-\mathsf{w})^2} \quad (29)$$

$$\mathcal{E}_{c,J=1}^{\mathsf{w},\text{DD}}(n^{\mathsf{w}}) \approx \frac{\mathsf{w}(1-3\mathsf{w})}{(1-\mathsf{w})^2}, \mathcal{E}_{c,J=1}^{\mathsf{w},\overline{\text{DD}}}(n^{\mathsf{w}}) \approx -\frac{2\mathsf{w}^2}{(1-\mathsf{w})^2}. \quad (30)$$

As readily seen from Eqs. (29) and (30), individual correlation energies within an ensemble can be positive. This is not surprising as the energy extraction procedure used in Eq. (10) is *not* variational, even though the ensemble energy is. We also clearly see that, in both decompositions, density-driven correlations can be substantial. In the equiensemble ($\mathsf{w} = 1/2$) case, the density- and state-driven correlation energy ratio equals 50% and 66% in the first and second decompositions, respectively. We essentially reach the same conclusions as Gould and Pittalis [32], even though we use a different decomposition. Turning to the $\overline{\text{SD}}$-$\overline{\text{DD}}$ decomposition of the ensemble correlation energy, the following expression is obtained in the regime under study [39]:

$$\mathcal{E}_{c}^{\mathsf{w},\overline{\text{SD}}}(n^{\mathsf{w}}) \approx -\frac{1}{2\eta^2}(1-\mathsf{w}) + \frac{\mathsf{w}^2(1+5\mathsf{w})}{2(1-\mathsf{w})^2}, \quad (31)$$

$$\mathcal{E}_{c}^{\mathsf{w},\overline{\text{DD}}}(n^{\mathsf{w}}) \approx -\frac{\mathsf{w}^2(1+\mathsf{w})}{(1-\mathsf{w})^2}, \quad (32)$$

while the density functional approximations introduced previously give

$$\mathcal{E}_{c}^{\mathsf{w},\overline{\text{SD}}}(n^{\mathsf{w}}) \overset{\text{GSC}\overline{\text{SD}}}{\approx} -\frac{1}{2\eta^2}(1-\mathsf{w}), \quad (33)$$

$$\mathcal{E}_{c}^{\mathsf{w},\overline{\text{DD}}}(n^{\mathsf{w}}) \overset{\text{GSX}\overline{\text{DD}}}{\approx} -\mathsf{w}^2[1+2\mathsf{w}(1-\mathsf{w})]. \quad (34)$$

As we used exact densities, density-driven errors [16] have been neglected. Their study is left for future work. Around the leading (second) order in $1/\eta \gg 1$, which is correctly reproduced within the simple GSC$\overline{\text{SD}}$ approximation, both $\overline{\text{SD}}$ and $\overline{\text{DD}}$ correlations contribute (almost equally in the equiensemble case) to the ensemble correlation energy, but with opposite sign, thus reducing substantially the weight dependence [see Eqs. (31) and (32)]. While an accurate description of the $\overline{\text{DD}}$ correlation on top of GSC$\overline{\text{SD}}$ overestimates the total correlation energy, a drastic improvement is obtained by combining the GSX$\overline{\text{DD}}$ with GSC$\overline{\text{SD}}$, thanks to error cancellations [see the Supplemental Material [39] for further details]. This promising result might be further improved by incorporating $\overline{\text{SD}}$ correlations from the excited state, which is left for future work.

Summary and outlook.—By uncovering the individual correlation energies within a density functional ensemble, we were able to derive a state- and density-driven decomposition of the ensemble correlation where, unlike in the Gould-Pittalis decomposition [32], no additional state-specific KS system is needed. By expressing the density-driven ensemble correlation energy in terms of the ensemble weights, the ensemble KS orbitals, and their (static) linear response to variations in the weights, we made a crucial step toward the development of first-principle density functionals for ensembles. While we focused on individual energies, the extension of the theory to energy couplings such as transition dipole moments or nonadiabatic couplings is highly desirable. Work is currently in progress in these directions.

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