

Correlation energies of many-electron ensembles are more than the sum of their parts

Tim Gould

Old Micro- and Nanotechnology Centre, Griffith University, Nathan, Qld 4111, Australia

Stefano Pittalis

CNR-Istituto di Nanoscienze, Via Campi 213A, I-41125 Modena, Italy

Density functional theory can be extended to excited states by means of a unified variational approach for passive state ensembles. This extension overcomes the restriction of the typical density functional approach to ground states, and offers useful formal and demonstrated practical benefits. The correlation energy functional in the generalized case acquires higher complexity than its ground state counterpart, however. Little is known about its internal structure nor how to effectively approximate it in general. Here we demonstrate that such a functional can be broken down into natural components, including what we call “state-” and “density-driven” correlations, with the latter being a unique feature of ensembles. Such a decomposition, summarised in eq. (10), is exact and also provides us with a pathway to general approximations.

Electronic structure theory has transformed the study of chemistry, materials science and condensed matter physics, by enabling quantitative predictions using computers. But a general solution to the many-electron problem remains elusive, because the electron-electron interactions imply highly non-trivial correlations among the relevant degrees of freedoms. Out of the numerous electronic structure methodologies, density functional theory [1–3] (DFT) has become the dominant approach thanks to its balance between accuracy and speed, achieved by using the electron density as the basic variable, then mapping the original interacting problem onto an auxiliary non-interacting problem.

DFT gives access to ground states, but not excited states, meaning alternatives must be used for important processes like photochemistry or exciton physics [4]. Its time-dependent extension (TDDFT) does offer access to excited states at reasonable cost [5, 6], and is thus commonly employed for this purpose. Routine applications of TDDFT reuse ground-state approximations by evaluating them on the instantaneous density, the so-called adiabatic approximation. This approach fails badly, however, when many-body correlations defy a time-dependent mean-field picture, including for important charge transfer excitations [7, 8].

One highly promising alternative involves tackling both ground and excited eigenstates by means of one and the same density functional approach [9–11], using ensemble DFT (EDFT). EDFT is appealing because it can automatically deal with otherwise difficult orthogonality conditions and can potentially tap into more than 30 years of density functional approximation development. EDFT has been shown to solve problems that are difficult for TDDFT, such as charge transfers, double excitations, and conical intersections [12–22].

Consolidating the preliminary success of EDFT into useful approximations requires further understanding of how many-body correlations get encoded in EDFT and how they can be approximated generally. The correlation

energy of many-electron ground states is traditionally divided into dynamical (weak) and static (strong) correlations. This decomposition is by no means unambiguous, yet is very useful both for designing, and understanding the limitations of, approximations [23]. Both static and dynamic correlations are also present in ensembles. But the internal structure of the correlation energy functional for ensembles is, by necessity, more complex. Little is known about its specific properties and quirks.

In this Letter, we therefore introduce a decomposition of the ensemble correlation energy that lends itself both to an exact evaluation *and* to a universal approximation scheme. This decomposition uncovers a particular kind of correlation which is unique to EDFT – *density-driven correlations* – which has so far gone unnoticed, and which is similar to, but not the same as density-driven errors of approximations [24]. **Ultimately, these components appear because the Kohn-Sham scheme in EDFT provides the exact overall ensemble particle density, but not the density of each state in the ensemble.** Our approach makes use of recent results on the Hartree-exchange component of the ensemble energy [25] and introduces a generalization of the Kohn-Sham machinery, which is also presented here. We shall describe our construction first formally and then also by means of direct applications. In doing so, we provide estimates of the magnitude of the various correlation components in prototypical cases. The relevance of the density-driven correlation is thus established unambiguously.

A primer on EDFT: For a given electron-electron interaction strength λ , external potential v , and set of weights \mathcal{W} one can find an ensemble density matrix, $\hat{\Gamma}^\lambda[v; \mathcal{W}] = \sum w_\kappa |\kappa^\lambda\rangle \langle \kappa^\lambda|$, via [9]

$$\hat{\Gamma}^\lambda[v; \mathcal{W}] \equiv \arg \min_{\hat{\Gamma}} \text{Tr} \left[\hat{\Gamma} \hat{H}^\lambda[v] \right] \equiv \sum_{\kappa} w_{\kappa} E_{\kappa}^{\lambda}[v]. \quad (1)$$

Here $\mathcal{W} = \{w_{\kappa}\}$ describes a set of non-negative weights that obey $\sum_{\kappa} w_{\kappa} = 1$. A consequence of (1) is that $|\kappa^\lambda\rangle$ are eigenfunctions of $\hat{H}^\lambda[v] = \hat{T} + \lambda \hat{W} + \int \hat{n}(\mathbf{r}) v(\mathbf{r}) d\mathbf{r}$

sorted so that $w_\kappa \leq w_{\kappa'}$ for eigenvalues $E_\kappa^\lambda > E_{\kappa'}^\lambda$, where $E_\kappa^\lambda = \langle \kappa | \hat{H} | \kappa \rangle$, making the ensemble a passive state, i.e. one from which no work can be extracted [26]. We can, without loss of generality, assign equal weights whenever interacting states are degenerate. [27] Then, $n^\lambda[v; \mathcal{W}] \equiv \text{Tr}[\hat{\Gamma}^\lambda[v; \mathcal{W}] \hat{n}(\mathbf{r})]$ defines a unique functional of v and \mathcal{W} .

By the Gross-Oliveira-Kohn (GOK) theorems [9–11] and the usual assumption that all densities of interest are ensemble v -representable, there exists a potential

$$v^\lambda[n; \mathcal{W}] \equiv \arg \max_u \left\{ \sum_\kappa w_\kappa E_\kappa^\lambda[u] - \int n u d\mathbf{r} \right\} \quad (2)$$

that is a unique functional of n and \mathcal{W} . Notice here we allow λ to vary while keeping n constant to connect “adiabatically” the non-interacting ($\lambda = 0, v^0 \equiv v_s$) with the fully interacting limits ($\lambda = 1, v^1 \equiv v$). This lets us define the universal functional

$$\mathcal{F}^\lambda[n] \equiv \sum_\kappa w_\kappa \langle \kappa^\lambda | \hat{T} + \lambda \hat{W} | \kappa^\lambda \rangle \equiv \text{Tr}[\hat{\Gamma}^\lambda(\hat{T} + \lambda \hat{W})] \quad (3)$$

where $|\kappa^\lambda\rangle$ are eigenstates of $[\hat{T} + \lambda \hat{W} + \hat{v}^\lambda] |\kappa^\lambda\rangle = E_\kappa^\lambda |\kappa^\lambda\rangle$, $\hat{\Gamma}^\lambda = \sum w_\kappa |\kappa^\lambda\rangle \langle \kappa^\lambda|$ and $\text{Tr}[\hat{\Gamma}^\lambda \hat{n}] = \sum w_\kappa \langle \kappa^\lambda | \hat{n} | \kappa^\lambda \rangle = n$. For brevity, we now drop explicit references to \mathcal{W} .

The KS kinetic energy \mathcal{T}_s is a density functional defined by the special case $\lambda = 0$, in which interactions \hat{W} are switched off completely. Eq. (3) gives

$$\mathcal{T}_s[n] \equiv \mathcal{F}^0 = \sum w_\kappa \langle \kappa^0 | \hat{T} | \kappa^0 \rangle = \sum w_\kappa T_{s,\kappa}, \quad (4)$$

where $|\kappa^0\rangle$ are orthogonal KS eigenstates of $\hat{H}^0 = \hat{T} + \int \hat{n} v^0[n] d\mathbf{r}$. For simplicity, we focus on cases for which the degeneracy only involves the spin-degree of freedoms, not the orbital part – this is sufficient for elucidating the main points of this work. This lets us choose states $|\kappa^0\rangle$ that are Slater determinants of one-particle orbitals $\phi_i[n](\mathbf{r})$, specified by their occupation factors $\theta_{i\sigma}^\kappa \in \{0, 1\}$ for orbital i in spin σ . The orbitals obey $[\hat{t} + v^0] \phi_i[n; \mathbf{r}] = \epsilon_i[n] \phi_i[n; \mathbf{r}]$. Note that, by definition of $v^\lambda[n]$, we get $n = \sum_\kappa w_\kappa n_\kappa = \sum_\kappa w_\kappa n_{s,\kappa}$, where $n_\kappa \equiv \langle \kappa^1 | \hat{n} | \kappa^1 \rangle$ and $n_{s,\kappa} \equiv \langle \kappa^0 | \hat{n} | \kappa^0 \rangle$. The determinants then give, $n_{s,\kappa} = \sum_i \theta_{i\sigma}^\kappa |\phi_i|^2$ so that $n = \sum_i f_i |\phi_i|^2$ where $0 \leq f_i = \sum_\kappa w_\kappa \theta_{i\sigma}^\kappa \leq 2$ [here $\theta_i = \sum_\sigma \theta_{i\sigma}$].

The difference $\mathcal{E}_{\text{Hxc}}[n] = \mathcal{F}^1[n] - \mathcal{T}_s[n]$ accounts for the electron-electron interaction beyond the Kohn-Sham kinetic energy. Gould and Pittalis [25] recently showed that the ensemble Hartree-exchange energy:

$$\mathcal{E}_{\text{Hx}}[n] \equiv \lim_{\lambda \rightarrow 0^+} \frac{\mathcal{F}^\lambda[n] - \mathcal{F}^0[n]}{\lambda} = \sum_\kappa w_\kappa \Lambda_{\text{Hx},\kappa}[n], \quad (5)$$

is of a similar form to (4), with the difference that terms $\Lambda_{\text{Hx},\kappa}$ can involve contributions from superpositions of different determinants $|\kappa^0\rangle$: $\Lambda_{\text{Hx},\kappa}[\{\phi_i\}] = \langle \kappa^{0+} | \hat{W} | \kappa^{0+} \rangle$. Here, $|\kappa^{0+}\rangle = \sum_{\kappa'} U_{\kappa\kappa'} |\kappa^0\rangle$ is taken over Slater determinants with different spin configurations, that are degenerate both in particle density and kinetic energy. Thus,

$|\kappa^{0+}\rangle$ can be regarded as valid non-interacting KS (yet multi-determinant) states obeying $\langle \kappa^{0+} | \hat{n} | \kappa^{0+} \rangle = n_{s,\kappa}$ and $\langle \kappa^{0+} | \hat{T} | \kappa^{0+} \rangle = T_{s,\kappa}$.

To complete the picture, we can further define the correlation energy functional

$$\mathcal{E}_c[n] := \mathcal{F}^1[n] - \mathcal{F}^{\text{EXX}}[n], \quad (6)$$

as the difference between the unknown \mathcal{F}^1 and the known exact exchange (EXX) functional $\mathcal{F}^{\text{EXX}} \equiv \mathcal{T}_s + \mathcal{E}_{\text{Hx}}$. While formally correct, the above expression serves little use in practice. In what follows, we shall introduce what we argue is a more useful expression for $\mathcal{E}_c[n]$.

Moving toward this objective, it is important to note that the KS densities $n_{s,\kappa}$ are not the same as the densities of interacting states n_κ . As an example, consider the lowest lying triplet (ts) and singlet (ss) excited states in H_2 . The KS densities of the singlet and triplet excitation are equal to each other while the interacting ones are not, i.e. $n_{s,\text{ts}} = n_{s,\text{ss}}$ and $n_{\text{ts}} \neq n_{\text{ss}}$ [21]. The same overall ensemble density is, by construction, obtained from the KS and the real ensemble. This fact is not specific to H_2 , and its implications for the general structure of the correlation energy of ensembles forms the bulk of the remainder of this letter. We shall first proceed formally, and then review and test key results in concrete cases.

State- and density-driven ensemble correlations: First, it is useful to recall that the energy components can be restated from functionals of n into functionals of the (ensemble) KS potential. As mentioned above, $\Lambda_{\text{Hx},\kappa}$ depends on the same set of single-particle orbitals as $T_{s,\kappa}$ and $n_{s,\kappa}$. Thus, they can all be transformed into a functional of a potential, by replacing $\phi_i[n]$ by $\psi_i[v_s] \equiv \phi_i[n[v_s]]$, where $[\hat{t} + v_s] \psi_i[v_s] = \epsilon_i[v_s] \psi_i[v_s]$. Therefore, given a functional of the single-particle orbitals, we can readily express it as a functional of the KS potential; such as $n_{s,\kappa}[v_s] \equiv \sum_i \theta_{i\sigma}^\kappa |\psi_i[v_s]|^2$, and, similarly, for $T_{s,\kappa}[v_s]$ and $\Lambda_{\text{Hx},\kappa}[v_s]$.

As a second and crucial step, we admit that the KS procedure can be extended in such a way that for any state $|\kappa\rangle$, we can find at least one potential v_s^κ such that $n_{s,\kappa}[v_s \rightarrow v_s^\kappa] = n_\kappa$ is the resulting density. Although there may be multiple potentials that give the density (i.e., $v_s^\kappa \rightarrow n_\kappa$), the bi-functional

$$v_s^\kappa[n_\kappa, n] \equiv \arg \min_{v_s^\kappa \rightarrow n_\kappa} \int d\mathbf{r} n |v_s[n] - v_s^\kappa|, \quad (7)$$

selects v_s^κ as the potential yielding n_κ that is closest to the KS potential yielding n .

Once v_s^κ is determined, we introduce

$$\bar{T}_{s,\kappa}[n_\kappa, n] \equiv T_{s,\kappa}[v_s \rightarrow v_s^\kappa[n_\kappa, n]], \quad (8)$$

$$\bar{\Lambda}_{\text{Hx},\kappa}[n_\kappa, n] \equiv \Lambda_{\text{Hx},\kappa}[v_s \rightarrow v_s^\kappa[n_\kappa, n]], \quad (9)$$

where the original functionals are transformed by replacing the KS orbitals $\psi_i[v_s] \rightarrow \psi_i[v_s^\kappa]$ in the orbital

functionals, to give energy bifunctionals of the specific density n_κ and the total ensemble density n . We thus extend all key functionals to be specified for ensemble density components, as well as globally. For the special case $n_\kappa = n_{s,\kappa}$ we are guaranteed to find $v_s^\kappa[n_{s,\kappa}, n] = v_s$ by construction. It then follows that $\mathcal{T}_s[n] = \sum_\kappa w_\kappa \bar{T}_{s,\kappa}[n_{s,\kappa}, n]$, $\mathcal{E}_{\text{HX}}[n] = \sum_\kappa w_\kappa \bar{\Lambda}_{\text{HX},\kappa}[n_{s,\kappa}, n]$.

Finally, we can express $\mathcal{E}_c[n]$ as follows:

$$\mathcal{E}_c[n] \equiv \sum_\kappa w_\kappa \{ \bar{E}_{c,\kappa}^{\text{SD}}[n_\kappa, n] + \bar{E}_{c,\kappa}^{\text{DD}}[n_\kappa, n] \}. \quad (10)$$

Here, the state-driven (SD),

$$\bar{E}_{c,\kappa}^{\text{SD}}[n_\kappa, n] := \bar{F}_\kappa^1[n_\kappa, n] - \bar{F}_\kappa^{\text{EXX}}[n_\kappa, n], \quad (11)$$

and density-driven (DD),

$$\bar{E}_{c,\kappa}^{\text{DD}}[n_\kappa, n] := \bar{F}_\kappa^{\text{EXX}}[n_\kappa, n] - \bar{F}_\kappa^{\text{EXX}}[n_{s,\kappa}, n] \quad (12)$$

terms are defined using

$$\begin{aligned} \bar{F}_\kappa^1[n_\kappa, n] &:= E_\kappa[n] - \int dr n_\kappa(\mathbf{r}) v[n](\mathbf{r}), \\ \bar{F}_\kappa^{\text{EXX}}[n_\kappa, n] &:= \bar{T}_{s,\kappa}[n_\kappa, n] + \bar{\Lambda}_{\text{HX},\kappa}[n_\kappa, n]. \end{aligned}$$

Eq. (10) is the key result of the present work. It expresses the correlation energy of GOK ensembles in terms of: a) state-driven correlations i.e., a weighted average over terms shown in (11) which are like the usual pure state correlation energy, but here involve bifunctionals of $[n_\kappa, n]$; and b) density-driven correlations, i.e., a weighted average over terms shown in (12), which resemble difference between exact exchange energies at different pure state densities. Note that in a pure state (ground-state) system, $n_{s,0} = n_0 = n$ and thus $\mathcal{E}_c^{\text{DD}} = 0$, as expected. Density-driven correlations are consequently a unique feature of ensemble DFT.

Implications: First of all, we stress that our decomposition does not necessitate handling directly highly problematic spurious (either self- or ghost-) interactions [28–30]. Because, our correlation functional is defined on top of an ensemble Hartree-exchange which is already maximally free from such interactions. Any spurious interactions present must thus be the result of approximation. Our decomposition, of course, is not meant to tame unavoidable strong correlations.

We now turn to how our scheme can help in the development of new approximations. Inspired by the principle of minimal effort, one might seek to replace the entire correlation energy with the SD terms, eq. (11), by reusing any standard DFT approximation, i.e. set $E_{c,\kappa}^{\text{SD}}[n_\kappa, n] \rightarrow E_c^{\text{DFA}}[n_\kappa]$. Such a proposal is not new in EDFT and with appropriate care has been shown to give good results in excited state and related non-integer ensembles [13, 28, 31]. But now we can finally appreciate what is neglected by using such a simplified approach.

Not only is the additional functional dependence on n disregarded, but also the corresponding DD correlations, eq. (12), are entirely ignored.

Our next concern is to determine how important these missing terms are. As we shall show, the DD correlation energy is non-negligible in the prototypical cases we study. Consequently, there is a need to account for it when devising new, EDFT-specific functionals.

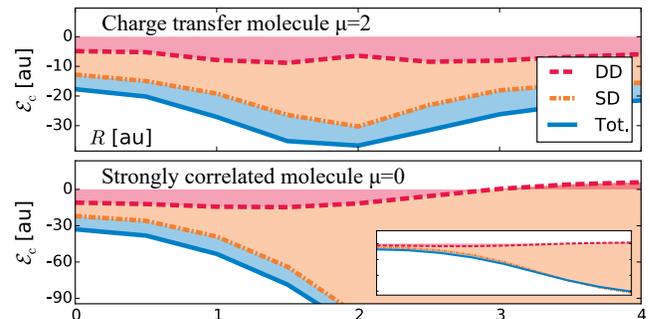


FIG. 1. Decomposition of the correlation energy of the charge transfer (top) and strongly-correlated (bottom) cases. The shaded regions show the relative significance of density-driven and state-driven correlations, with the former contributing approximately one quarter of the total correlation energy in the charge transfer case. The inset of the bottom panel shows the unzoomed plot. Here we set a mixture of 60/30/10% respectively for the three lowest energy states.

Applications: Having established the basic theory, let us now study the role of density-driven correlations in some examples: two electron soft-Coulomb molecules. These numerically solvable one-dimensional molecules have electron-electron interactions $W(x) = (\frac{1}{4} + x^2)^{-\frac{1}{2}}$ and external potential $v(x) = W(x+R/2) + W(x-R/2) - \mu e^{-(x-R/2)^2}$ for nuclear distance R , to give a Hamiltonian $\hat{H} = -\frac{1}{2}[\partial_{x_1}^2 + \partial_{x_2}^2] + W(x_1 - x_2) + v(x_1) + v(x_2)$. By tuning μ , the molecules can exhibit chemically interesting properties such as charge transfer excitations ($\mu = 2$) or strong correlations ($\mu = 0$) [21].

We restrict ourselves to ensembles involving the ground- (gs), triplet-excited (ts) and singlet-excited (ss) states only. We perform our calculations in three steps:

1. Solve the two electron Hamiltonian \hat{H} with one- and two-body interactions terms to obtain interacting state-specific terms $E_\kappa, |\kappa\rangle, n_\kappa, F_\kappa^1 = \langle \kappa | \hat{T} + \hat{W} | \kappa \rangle = E_\kappa - \int dx n_\kappa(x) v(x)$, for the three states $\kappa \in \{\text{gs, ts, ss}\}$, and ensemble averages therefrom, e.g., $n = \sum_\kappa w_\kappa n_\kappa$ and $\mathcal{F}^1 = \sum_\kappa w_\kappa F_\kappa^1$.
2. Invert the density using the single-particle orbital Hamiltonian $\hat{h} = -\frac{1}{2}\partial_x^2 + v(x)$ to find $v(x) = v_s(x) \rightarrow n(x)$ and real orbitals ϕ_0 and ϕ_1 that are required for the KS eigenstates. Here, v_s depends on the density n and groundstate weight w_{gs} only, as $n = (1 + w_{\text{gs}})\phi_0^2 + (1 - w_{\text{gs}})\phi_1^2$. From these terms,

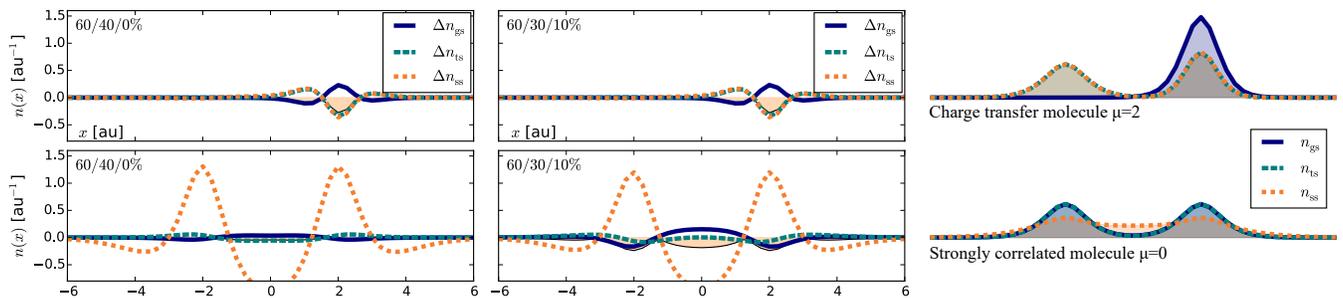


FIG. 2. Density differences for charge transfer (top) and strongly-correlated (bottom) cases, and with only triplet states (left) or with singlet states as well (centre). The line plots show $5\times$ the density difference for each state (navy, teal and orange dashed lines), and the cream shaded area shows $-5\times$ the weighted average absolute density difference $\Delta|n|$. The final panel (right) shows the true densities of the three states, for visual comparison.

calculate $n_{s,\kappa}$, $T_{s,\kappa}$ and $\Lambda_{\text{Hx},\kappa}$, and ensemble averages, again for $\kappa \in \{\text{gs}, \text{ts}, \text{ss}\}$. Here, $T_{s,\text{ts}} = T_{s,\text{ss}}$ and $n_{s,\text{ts}} = n_{s,\text{ss}}$ but $\Lambda_{\text{Hx},\text{ts}} \neq \Lambda_{\text{Hx},\text{ss}}$.

- Carry out separate inversions using $n_{\text{gs}} = 2\psi_0[v_s^{\text{gs}}]^2$, $n_{\text{ts}} = \psi_0[v_s^{\text{ts}}]^2 + \psi_1[v_s^{\text{ts}}]^2$ and $n_{\text{ss}} = \psi_0[v_s^{\text{ss}}]^2 + \psi_1[v_s^{\text{ss}}]^2 \neq n_{\text{ts}}$ to obtain the three potentials v_s^κ . By all indications these are unique as the inversion routine smoothly approaches a solution in all cases. Then use the resulting orbitals $\psi_0[v_s^\kappa]$ and $\psi_1[v_s^\kappa]$ to calculate $\bar{T}_{s,\kappa}[n_\kappa, n]$ and $\bar{\Lambda}_{\text{Hx},\kappa}[n_\kappa, n]$ on the interacting densities of the three states, and thus obtain the final ingredients for eqs (10)–(12).

In Figure 1 we show the correlation energy for two examples of bond breaking (which occurs at $R \approx 3$), resolved into total, DD and SD components. One example exhibits charge transfer excitations (top) with $\mu = 2$, and the other involves strong correlations (bottom) with $\mu = 0$. We choose an ensemble with 60% groundstate, 30% triplet state and 10% singlet state (60/30/10%).

The first thing to notice is that in the “typical” charge transfer case, the DD correlations form a substantial portion of the total correlation energy, about 25% on average. This highlights the importance of capturing, or approximating it somehow: a raw application of even a nearly perfect approximation to the SD correlations will miss around one quarter of the correlation energy. The strongly correlated case has a similar breakdown for small R , but becomes dominated by the SD correlations for large R (see especially the inset). This is not surprising, as the SD term captures the multi-reference physics that gives rise to most of the correlation energy, whereas the DD term contains only weaker dynamic correlations.

Of final note, close inspection of the strongly correlated case reveals a subtle point: for $R \geq 3$, the DD correlation energy is *positive*. At first glance this might seem to be impossible – correlation energies should always be negative. However, it reflects the fact that the DD correlation energy is defined via an energy difference between

two states which come from different many-body problems with different densities. Thus, the negative sign is not guaranteed by any minimization principle.

Next, we turn to the densities of the two cases above, which we show in Figure 2 for $R = 4$. As above, we evaluate the 60/30/10% case (middle), but we also include a 60/40/0% case (left) without any singlet contribution, to uncover the role of the weights on the densities. We show density differences $\Delta n_\kappa = n_{s,\kappa} - n_\kappa$ between KS and true states in the left and middle panels, and the true densities at the right. We also show the weighted mean absolute density difference $\Delta|n| = \sum_\kappa w_\kappa |\Delta n_\kappa|$, to visually summarise the density difference that may affect the energy, keeping in mind that $\sum_\kappa w_\kappa \Delta n_\kappa = 0$. In all cases it is clear that the density differences are substantial.

One particularly interesting feature is that the strongly correlated case (bottom) shows fundamentally different deviations when the singlet is neglected or included, reflecting the large errors $n_{s,\text{ts}} - n_{\text{ts}}$ and $n_{s,\text{ss}} - n_{\text{ss}}$ in simultaneously trying to represent the triplet and singlet states using $n_{s,\text{ts}} = n_{s,\text{ss}} = \phi_0^2 + \phi_1^2$. Any calculation of ensembles involving the three lowest energy configurations will need to handle such a difficult case via a direct DD correlation energy approximation.

Finally, we note that the results reported here can be directly generalized to show that density-driven terms will also feature in other ensemble theories, such as for non-integer electron number [32], using the LEXX functional for Hx [33]. The relationship between the two approaches, and a recently introduced unified approach [34], will be investigated in future works.

To conclude, it is clear from our construction, exemplified in eq. (10), and from our illustrative examples, that the density-driven correlation energy is an important part of the correlation energy \mathcal{E}_c of ensembles. An apparent advantage of our approach is that it does not require us to deal with the disastrous ghost interactions, that can be avoided already at the Hartree-exchange level. Our results shows that direct transfer of existing

DFT approximations to ensembles – which can be done on state-driven components only – will miss the density-driven part of the correlation energy that contributes up to 30% of \mathcal{E}_c , in our examples.

The correlation energies of many-electron ensembles are more than a straightforward sum of their state components. Thus, future ensemble density functional approximations must find some way to systematically account for the terms revealed in this work, in a low-cost fashion. Work is ongoing to establish what role these terms contribute in more realistic systems, and whether or not simple approximations might deal with them.

S.P. acknowledges partial support from EU Centre of Excellence MaX-Materials at the eXascale (H2020-EINFRA 2015, grant No. 676598).

-
- [1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- [2] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- [3] R. O. Jones, Rev. Mod. Phys. **87**, 897 (2015).
- [4] S. Matsika and A. I. Krylov, Chem. Rev. **118**, 6925 (2018).
- [5] E. Runge and E. K. Gross, Phys. Rev. Lett. **52**, 997 (1984).
- [6] M. E. Casida and M. Huix-Rotllant, Annu. Rev. Phys. Chem. **63**, 287 (2012).
- [7] C. A. Ullrich and I. V. Tokatly, Phys. Rev. B **73**, 235102 (2006).
- [8] N. T. Maitra, J. Phys.: Cond. Matter **29**, 423001 (2017).
- [9] E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A **37**, 2805 (1988).
- [10] E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A **37**, 2809 (1988).
- [11] L. N. Oliveira, E. K. U. Gross, and W. Kohn, Phys. Rev. A **37**, 2821 (1988).
- [12] M. Filatov and S. Shaik, Chem. Phys. Lett. **304**, 429 (1999).
- [13] M. Filatov, M. Huix-Rotllant, and I. Burghardt, The Journal of chemical physics **142**, 184104 (2015).
- [14] M. Filatov, WIREs Comput. Mol. Sci. **5**, 146 (2015).
- [15] M. Filatov, “Ensemble DFT approach to excited states of strongly correlated molecular systems,” in *Density-Functional Methods for Excited States*, edited by N. Ferré, M. Filatov, and M. Huix-Rotllant (Springer International Publishing, Cham, 2016) pp. 97–124.
- [16] O. Franck and E. Fromager, Mol. Phys. **112**, 1684 (2014).
- [17] K. Deur, L. Mazouin, and E. Fromager, Phys. Rev. B **95**, 035120 (2017).
- [18] A. Pribram-Jones, Z.-h. Yang, J. R. Trail, K. Burke, R. J. Needs, and C. A. Ullrich, J. Chem. Phys. **140** (2014).
- [19] Z.-h. Yang, J. R. Trail, A. Pribram-Jones, K. Burke, R. J. Needs, and C. A. Ullrich, Phys. Rev. A **90**, 042501 (2014).
- [20] Z.-h. Yang, A. Pribram-Jones, K. Burke, and C. A. Ullrich, Phys. Rev. Lett. **119**, 033003 (2017).
- [21] T. Gould, L. Kronik, and S. Pittalis, J. Chem. Phys. **148**, 174101 (2018).
- [22] F. Sagredo and K. Burke, arXiv preprint arXiv:1806.03392 (2018).
- [23] S. Ghosh, P. Verma, C. J. Cramer, L. Gagliardi, and D. G. Truhlar, Chem. Rev. (2018).
- [24] M.-C. Kim, E. Sim, and K. Burke, Phys. Rev. Lett. **111**, 073003 (2013).
- [25] T. Gould and S. Pittalis, Phys. Rev. Lett. **119**, 243001 (2017).
- [26] M. Perarnau-Llobet, K. V. Hovhannisyan, M. Huber, P. Skrzypczyk, N. Brunner, and A. Acín, Phys. Rev. X **5**, 041011 (2015).
- [27] We must also assume that no occupied ($w_\kappa > 0$) levels cross as interaction strength λ is varied, i.e. that the energy ordering of low-lying states is adiabatically preserved, per Ref. 25. This is true in the cases considered here.
- [28] E. Pastorczak and K. Pernal, J. Chem. Phys. **140**, 18A514 (2014).
- [29] A. Pribram-Jones, Z.-h. Yang, J. R. Trail, K. Burke, R. J. Needs, and C. A. Ullrich, J. Chem. Phys. **140**, 18A541 (2014).
- [30] N. I. Gidopoulos, P. G. Papaconstantinou, and E. K. U. Gross, Phys. Rev. Lett. **88**, 033003 (2002).
- [31] E. Krausler and L. Kronik, Phys. Rev. Lett. **110**, 126403 (2013).
- [32] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. **49**, 1691 (1982).
- [33] T. Gould and J. F. Dobson, J. Chem. Phys. **138**, 014103 (2013).
- [34] B. Senjean and E. Fromager, arXiv preprint arXiv:1805.08715 (2018).