Double excitations from ensemble density functionals: theory and approximations

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Double excitations, which are dominated by a Slater-determinant with both electrons in the highest occupied molecular orbital promoted to the lowest unoccupied orbital(s), pose significant challenges for low-cost electronic structure calculations based on density functional theory (DFT). Here, we demonstrate that recent advances in ensemble DFT [*Phys. Rev. Lett.* **125**, 233001 (2020)], which extend concepts of ground-state DFT to excited states via a rigorous physical framework based on the ensemble fluctuation-dissipation theorem, can be used to shed light on the double excitation problem. We find that the exchange physics of double excitations is reproducible by standard DFT approximations using a linear combination formula, but correlations are more complex. We then show, using selected test systems, that standard DFT approximations may be adapted to tackle double excitations based on theoretically motivated simple formulae that employ ensemble extensions of expressions that use the on-top pair density.

Within molecular orbital theory, a *double excitation* refers to a many-electron state that is dominated by a doubly excited Slater determinant. [1] This definition somewhat depends on the single-particle basis being used as a reference, but it is sufficiently evocative to point out that this type of excitation entails a *double challenge* for present-day low-cost electronic structure methodologies based on density functional theory (DFT).

DFT [2, 3] is exact in principle but almost always approximated in practice using exchange-correlation energy models. Still, sophisticated density functional approximations (DFAs) are sufficiently accurate to power many studies of ground states due to an excellent quality to cost ratio. [4, 5] The *first challenge* for double excitations is that, unlike some triplets which may be regarded as a naturally "constrained" ground state, [6] doubly excited target states must be lowest in energy *and* orthogonal both to the actual ground state and any lower excited singlet. This places them beyond the reach of ground state functional forms. DFT's time-dependent counterpart [7] (TDDFT) does provide a theoretically rigorous way to deal with excitations. However, the *second challenge* for double excitations is that their prediction using TDDFT requires a highly non-trivial frequency dependence in the "kernel" DFA, which is extremely difficult to obtain in practice. [8–10] In contrast, ensemble DFT for excited states (EDFT) [11–13] has shown promise on model double excitations [14–16] and as a useful framework for wavefunction-based methodologies. [17–20]

In this Letter, we employ recent theory advances concerning the structure of exact ensemble functionals [21–25] with the goal of building high-quality general purpose ensemble DFA (EDFA) that can predict double excitation energies. Firstly, we show that exact ensemble exchange ('x') expressions acquire unexpected forms on double excitations. Importantly, this reveals that exchange can be tackled via straightforward re-use of stan-

dard DFAs. Secondly, we extend the random-phase approximation (RPA) to ensembles, to scrutinize limitations of existing correlation ('c') DFAs and to provide a strategy to re-use them. Thirdly, we put together all the gained insights to generate approximations for the overall ensemble 'Hxc' as a functional of the ensemble particle density and, explicitly, of the corresponding ensemble on-top pair-correlation function. Lastly, we demonstrate that EDFAs based on these results are competitive against prominent wavefunction-based alternatives.

We begin by listing the singlet states, $|S_k\rangle$, we are interested in: a ground state, $|S_0\rangle$, a singly excited state, $|S_1\rangle$, and a doubly excited state, $|S_2\rangle$. [26] We mix these three states in an ensemble,

$$\hat{\Gamma} = w_{S_0}|S_0\rangle\langle S_0| + w_{S_1}|S_1\rangle\langle S_1| + w_{S_2}|S_2\rangle\langle S_2| . \quad (1)$$

whose average energy $\mathcal{E}[v] = \min_{\hat{\Gamma}} \mathrm{Tr}[\hat{\Gamma}(\hat{T} + \hat{W} + \hat{v})] = w_{S_0}E_{S_0} + w_{S_1}E_{S_1} + w_{S_2}E_{S_2}$ can be determined *variationally*, for any weights obeying $w_{S_0} \geq w_{S_1} \geq w_{S_2} \geq 0$. [11] Here, $\hat{T}$ is the kinetic energy operator, $\hat{W}$ is the electron-electron interaction operator and $\hat{v} = \int v(\boldsymbol{r})\hat{n}(\boldsymbol{r})d\boldsymbol{r}$ is the external potential operator defined using the density operator $\hat{n}$. Note that Eq. (1) easily generalizes to ensembles mixing degenerate states, where an essential general condition is to work with *totally* symmetric ensembles. [27] Note further that single and double excitation energies of the system can be computed by varying the weights, e.g. $E_{S_2} = \partial_{w_{S_2}}\mathcal{E}$.

Analogous to conventional DFT, we may equivalently write, $\mathcal{E} = \mathcal{T}_s + \mathcal{E}_{\mathrm{Hx}} + \mathcal{E}_{\mathrm{c}} + \int nvd\boldsymbol{r}$, where $\mathcal{T}_s$, $\mathcal{E}_{\mathrm{Hx}}$ and $\mathcal{E}_{\mathrm{c}}$ are the ensemble Kohn-Sham (KS) kinetic energy, Hartree-exchange ('Hx') and correlation density functionals, respectively. Our goal in this work is to devise DFAs for $\mathcal{E}_{\mathrm{Hx}}$ and $\mathcal{E}_{\mathrm{c}}$ that are accurate for double excitations. [28] To this end, let us first recall the ansatz-free definitions of these functionals: [22] $\mathcal{T}_s = \mathcal{F}^0$, $\mathcal{E}_{\mathrm{Hx}} = \lim_{\lambda \to 0^+} \frac{\mathcal{F}^\lambda - \mathcal{T}_s}{\lambda}$, and $\mathcal{E}_{\mathrm{c}} = \mathcal{F}^1 - \mathcal{T}_s - \mathcal{E}_{\mathrm{Hx}}$. [23] Here, we introduced the uni-

versal functional, $\mathcal{F}^\lambda[n] = \min_{\hat{\Gamma}_w \to n} \text{Tr}[\hat{\Gamma}_w(\hat{T} + \lambda\hat{W})]$, which adiabatically connects the non-interacting ($\lambda = 0$, $|S_{s,k}\rangle$) and interacting ($\lambda = 1$, $|S_k\rangle$) limits. [29]

A major advantage of EDFT over DFT is that the ensemble KS states are *non-interacting* configuration state functions (CSFs) rather than single Slater determinants; [22] i.e., *minimal* linear combinations of Slater determinants which are symmetry adapted both w.r.t. spin and spatial degrees-of-freedom. [30] Thus, interacting and KS states can be labeled by the same quantum numbers. For our initial example [see eq. (1)] we obtain, $\hat{\Gamma}_s = \sum_k w_{S_k}|S_{s,k}\rangle\langle S_{s,k}|$ with: $|S_{s,0}\rangle := |[c^2]h^2\rangle$ for the ground state; $|S_{s,1}\rangle := \frac{1}{\sqrt{2}}[|[c^2]h^\uparrow l^\downarrow\rangle + |[c^2]h^\downarrow l^\uparrow\rangle]$ for the state produced via a single excitation, $h \to l$, from the HOMO (h) to the LUMO (l); and $|S_{s,2}\rangle := |[c^2]l^2\rangle$ as the double excitation on $h \to l$. $[c^2] \equiv 1^2 \cdots (h-1)^2$ and restricted orbitals $\phi_{i\uparrow} = \phi_{i\downarrow}$ are employed throughout.

We then obtain $\mathcal{E}_{\text{Hx}} = \sum_{k=0}^2 w_{S_k}\langle S_{s,k}|\hat{W}|S_{s,k}\rangle$, which sums over the weighted contributions of KS-CSFs and is thereby free from spurious self and ghost interactions. But, it represents a *conjoint* 'Hx', which makes it difficult to reuse standard exchange('x')-DFAs directly. For example, the PBE0 hybrid functional approximation [31] sets $E_{\text{Hxc}}^{\text{PBE0}} := E_H + 0.25E_x^{\text{HF}} + 0.75E_x^{\text{PBE}} + E_c^{\text{PBE}} = E_{\text{Hx}} + 0.75(E_x^{\text{PBE}} - E_x^{\text{HF}}) + E_c^{\text{PBE}}$ using Hartree-Fock (HF) exchange, with PBE [32] exchange and correlation DFA.

Recently, a fluctuation-dissipation theorem (FDT) was extended and used to further resolve $\mathcal{E}_{\text{Hx}} := \mathcal{E}_H^{\text{FDT}} + \mathcal{E}_x^{\text{FDT}}$ into 'H' and 'x' energy expressions that are compatible with existing DFAs. [24] The same extension also offers insights into correlations, discussed further below. The key arguments of Ref. 24 may be summarized as follows: i) DFAs work because they capture universal and essential features of pair correlations; ii) one way to "ensemblize" these pair correlations from first principles is via the density-density response function χ of the ensemble; iii) the KS response, χ_s, allows us to define $\mathcal{E}_x^{\text{FDT}}$ in a way which is formally consistent with existing 'x'-DFA. $\mathcal{E}_H^{\text{FDT}}$ then includes all the remaining CSF terms; while state-driven correlation [23] can be handled by relating the KS to the interacting response function.

Using the above principles, we obtain $\mathcal{E}_H^{\text{FDT}} := \sum_{kk'} \min(w_{S_k}, w_{S_{k'}}) \int \frac{d\mathbf{r}d\mathbf{r}'}{2|\mathbf{r}-\mathbf{r}'|} n_s^{S_k S_{k'}}(\mathbf{r}) n_s^{S_{k'} S_k}(\mathbf{r}')$ with $n_s^{S_k S_{k'}} := \langle S_{s,k}|\hat{n}|S_{s,k'}\rangle$ for the 'H' functional; and

$$\mathcal{E}_x^{\text{FDT}} := -\frac{1}{2}\sum_{ij} f_{\max(i,j)}(ij|ji) \qquad (2)$$

for 'x', where the expression given above is a convenient corrolary of a result from Ref. 24 that is derived in Section I of the supplementary material [33] [SM-I]. Here, $f_i = \sum_k w_{S_k}\theta_i^{S_k}$ are the average occupations of orbital, ϕ_i, with occupation $\theta_i^{S_k} \in \{0,1,2\}$ in state S_k. This gives, $f_c = 2$ for all core ($c < h$) orbitals, $f_h = 2w_{S_0} + w_{S_1}$ for the HOMO and $f_l = w_{S_1} + 2w_{S_2}$ for the LUMO. $(ij|kl) := \int \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\phi_i^*(\mathbf{r})\phi_j(\mathbf{r}')\phi_k(\mathbf{r})\phi_l(\mathbf{r}')$.

Therefore, as a first step to work out a useful approximation we may use the *disjointed* 'x' to obtain,

$$\mathcal{E}_{\text{Hx}}^{\text{PBE0}} := \mathcal{E}_{\text{Hx}} + 0.75(\mathcal{E}_x^{\text{PBE}} - \mathcal{E}_x^{\text{FDT}}) . \qquad (3)$$

The details may, of course, be varied to cover other DFA including range-separated hybrids. The next crucial step is to break $\mathcal{E}_x^{\text{FDT}} := \sum_k w_k E_{x,S_k}^{\text{FDT}}$ into individual state contributions so that we can replace exact 'x' expressions by *existing* 'x'-DFA expressions. For this important task, we follow Fromager [25] to rigorously define,

$$E_{x,S_k}^{\text{FDT}} := \frac{\partial\mathcal{E}_x^{\text{FDT}}}{\partial w_{S_k}} = -\frac{1}{2}\sum_{ij}\theta_{\max(i,j)}^{S_k}(ij|ji) , \qquad (4)$$

where we used $f_{\max(i,j)} = \sum_k w_{S_k}\theta_{\max(i,j)}^{S_k}$ in eq. (2) to derive the second expression.

It follows from (4) that, $E_{x,S_0}^{\text{FDT}} = -\sum_{i,j\in\{c,h\}}(ij|ji) \equiv E_{x,S_0}^{\text{HF}}$, adopts its conventional HF form for the ground state – by construction. [24] Further algebraic manipulation of the above equations [SM-II] yields,

$$E_{x,S_1}^{\text{FDT}} = E_{x,T_0}^{\text{HF}} , \quad E_{x,S_2}^{\text{FDT}} = 2E_{x,T_0}^{\text{HF}} - E_{x,S_0}^{\text{HF}} \neq E_{x,S_2}^{\text{HF}} , \quad (5)$$

where both are defined in terms of conventional HF 'x' energies for lowest energy singlets, E_{x,S_0}^{HF}, and triplets, $E_{x,T_0}^{\text{HF}} = \langle[c^2]h^\uparrow l^\uparrow|\hat{W}|[c^2]h^\uparrow l^\uparrow\rangle = \langle[c^2]h^\downarrow l^\downarrow|\hat{W}|[c^2]h^\downarrow l^\downarrow\rangle = -\frac{1}{2}[\sum_{i,j\in\{c,h,l\}}(ij|ji) + \sum_{i,j\in\{c\}}(ij|ji)]$. Importantly, both $E_{x,S_0/T_0}$ have existing DFA counterparts. Also note that the corresponding 'H' energies, $E_{\text{H},S_k}^{\text{FDT}} := \partial_{w_{S_k}}\mathcal{E}_H^{\text{FDT}} = \partial_{w_{S_k}}[\sum_k w_{S_k}E_{\text{H},S_k}^{\text{HF}} + (w_{S_1} + w_{S_2})E_{ST}]$, involve $E_{\text{H},S_k}^{\text{HF}} := \int \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}n_s^{S_k S_k}(\mathbf{r})n_s^{S_k S_k}(\mathbf{r}')$ and $E_{ST} := 2(hl|lh)$ [SM-II]. Thus, $E_{\text{H},S_1/S_2}^{\text{FDT}} = E_{\text{H},S_1/S_2}^{\text{HF}} + E_{ST}$, contain the singlet-triplet splitting terms, E_{ST}, that are absent in $E_{x,S_1/S_2}^{\text{FDT}}$ but required by $E_{\text{Hx},S_k} = \langle S_{s,k}|\hat{W}|S_{s,k}\rangle = E_{\text{H},S_k}^{\text{FDT}} + E_{x,S_k}^{\text{FDT}}$.

Eq. (5) states two key results of this work. The first expression shows that single excitations have the same exchange formula, regardless of spin character, (S_1 vs any of T_0) – this result was previously used successfully, [34] but without derivation. The second expression is specific to this work and highlights the importance of ansatz-free procedures. Despite $|S_2\rangle$ being a single Slater determinant, the FDT 'x' of the lowest double excitation is not the same as HF 'x' energy. Rather, it is equivalent to the ground state HF 'x' of *twice a triplet minus a singlet*.

Finally, using eq. (5) in eq. (3) yields $\mathcal{E}_{\text{Hx}}^{\text{DFA}} := \mathcal{E}_{\text{Hx}} + \bar{\alpha}[(w_{S_0} - w_{S_2})(E_{x,S_0}^{\text{DFA}} - E_{x,S_0}^{\text{HF}}) + (w_{S_1} + 2w_{S_2})(E_{x,T_0}^{\text{DFA}} - E_{x,T_0}^{\text{HF}})]$ for the 'Hx' part of general hybrids [SM-II], where $\bar{\alpha} = 1 - \alpha$ is the complement to the Fock exchange fraction, α. The above analysis means we can *now reuse any existing* $E_{x,S_0/T_0}^{\text{DFA}}$ in $\mathcal{E}_{\text{Hx}}^{\text{DFA}}$. Previous work on single excitations successfully assumed [34] that E_{c,S_k}^{DFA} and E_{x,S_k}^{DFA} obey the same combination laws. If we extend this to

double excitations, we then obtain an 'Hxc' functional,

$$\mathcal{E}_{\text{Hxc}}^{\text{DFA}} := \mathcal{E}_{\text{Hx}} + (w_{S_0} - w_{S_2})\big[\bar{\alpha}(E_{\text{x},S_0}^{\text{DFA}} - E_{\text{x},S_0}^{\text{HF}}) + E_{\text{c},S_0}^{\text{DFA}}\big]$$
$$+ (w_{S_1} + 2w_{S_2})\big[\bar{\alpha}(E_{\text{x},T_0}^{\text{DFA}} - E_{\text{x},T_0}^{\text{HF}}) + E_{\text{c},T_0}^{\text{DFA}}\big] . \quad (6)$$

We revisit the extension below.

The above results can also be generalized to systems with D_l-fold degenerate LUMOs, such as Be, using ensembles of the form $\hat{\Gamma} = w_{S_0}|S_0\rangle\langle S_0| + w_{S_1}\hat{\Gamma}_{S_1} + w_{S_2}\hat{\Gamma}_{S_2}$, where $\hat{\Gamma}_{S_1}$ and $\hat{\Gamma}_{S_2}$ are themselves ensemble over an equal mixture of all degenerate excited states, to yield densities and effective potentials that preserve fundamental spatial symmetries. [27] In general, $E_{\text{Hx},S_k} := \frac{1}{2}\sum_{ij}[F_{ij}^{J,S_k}(ij|ij) + F_{ij}^{K,S_k}(ij|ji)]$, and $E_{\text{x},S_k}^{\text{FDT}} := -\frac{1}{2}\sum_{ij} f_{\max(i,j)}^{S_k}(ij|ji)$, where $F_{ij}^J = f_i f_j$ and $F_{ij}^K = -\frac{1}{2}F_{ij}^J$ except for pairs, $hh, hl_q, l_q h, l_q l_{q'}$, involving the HOMO, h, and/or one of the LUMOs, l_q. Values for $F^{J/K,S_k}$ and f^{S_k} are derived and reported in SM-II.
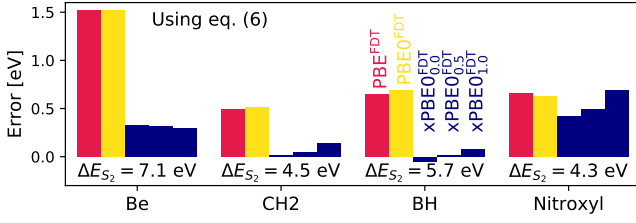

FIG. 1. Errors in excitation energy gaps (in eV) for the double excitation of Be, CH$_2$, BH and nitroxyl computed using FDT-derived PBE energy expressions [eq. (6)] with (PBE/PBE0, red/yellow) and without (xPBE$_\alpha$, navy) PBE correlations included. Reference values are provided as text.

Although eq. (6) is only slightly more complex than its ground state equivalent, evaluating it self-consistently for real molecular systems is much more difficult than the ground state problem, for practical reasons outlined in Ref. 35, and because of errors introduced by density-driven correlations, [23] which come from a failure to properly account for differences between KS and interacting excited state densities. To obtain the present results, we: i) set $w_{S_1} = 0$ in all calculations to restrict to mixtures of ground and doubly excited states only; [36] ii) optimize orbitals (mostly) via minimization over unitary transformations; [35] iii) Use the extrapolation procedure described in Ref. [34] to approximately remove density-driven correlation errors [23]. Full details in SM-III.

Figure 1 shows errors, $\Delta E_{S_2}^{\text{EDFA}} - \Delta E_{S_2}^{\text{ref}}$ in the resulting EDFA double excitation energies, $\Delta E_{S_2} := E_{S_2} - E_{S_0}$, of Be (where S_2 is five-fold degenerate), CH$_2$, BH (two-fold degenerate) and nitroxyl (ONH). Reference data is from Ref. 1 (Be and nitroxyl) and FCI results (CH$_2$ and BH) computed for this work. Energies are evaluated using eq. (6) for PBE [32] (red, $\alpha = 0$) and PBE0 [31] (yellow, $\alpha = 0.25$). Tests using other functionals [37, 38] are of slightly worse quality. Further technical details are given

in SM-III. Despite the rigorous theory behind the 'Hx' components in eq. (6), the results are uninspiring. This stands in contrast to the success of similar ensemblized DFA in predicting triplet and single excitations [34].

To understand why energies are so poor we first perform x-only PBE0-like (labeled xPBE0$_\alpha$ and defined via eq. (6) with $E_\text{c} = 0$, navy) calculations to investigate the contribution of exchange to the error. Two points are notable: 1) x-only FDT results depend only weakly on α, and the variation is larger with stronger correlations, which suggests that exchange physics is treated correctly at the density functional level. 2) Ensemble Hartree-Fock (HF) theory (xPBE$_1$) is rather accurate for Be, CH$_2$ and BH, suggesting that correlations cancel out in these systems, unlike in the DFA. Nitroxyl has strongly correlated ground and excited states so both failures and a wider variation of xPBE are expected. We therefore conclude that x-DFA (here, PBE) are reliable, and that the error comes primarily from the correlation functional.

As a natural next step, we seek to replicate the success of $\mathcal{E}_\text{x}^{\text{FDT}}$ by using the FDT [39] to tackle $\mathcal{E}_\text{c}$. Exact evaluation is impossible in general, so we instead invoke the random-phase approximation (RPA), [39–43] that has found widespread success in modelling difficult ground states; [41–43] and in providing constraints for popular DFAs for correlation. [44, 45] We ensemblize the RPA by using the same KS *ensemble* density-density response function used to derive eq. (2), [24]

$$\hat{\chi}_s(i\omega) = \sum_{ij} \frac{(f_i - f_j)(\epsilon_i - \epsilon_j)}{(\epsilon_i - \epsilon_j)^2 + \omega^2}\hat{\rho}_i\hat{\rho}_j , \quad (7)$$

$$\mathcal{E}_\text{c}^{\text{RPA}} := \int_0^\infty \frac{d\omega}{2\pi}\text{Tr}\big[\log(1 - \hat{\chi}_s\hat{W}) + \hat{\chi}_s\hat{W}\big] . \quad (8)$$

Eq. (8) thereby inherits an explicit dependence on the ensemble via the occupation factors, $\{f_i\}$. Here, ϵ_i is the KS eigenvalue of orbital, i; Tr and log indicate operator trace and logarithm; and $\text{Tr}[\hat{\rho}_i\hat{W}\hat{\rho}_j] = (ij|ji)$. Using (7) in (8) yields well-defined energies for $0 \leq f_l = w_{S_1} + 2w_{S_2} \leq 1$ and $f_h = 2 - f_l = 2w_{S_0} + w_{S_1}$ (note, $f_l > 1$ leads to negative values in the logarithm). Details of RPA calculations are in SM-IV.

Note that the frequency dependence in eq. (8) is averaged within an integration, rather than appearing pointwise as in the key linear-response TDDFT equations for excitations. This fact, together with explicit inclusion of double excitation effects in the ensemble response function, $\hat{\chi}_s$, overcomes memory-related issues [8] by letting us extend the RPA to double excitations, as below.

Figure 2 shows the ensemble RPA correlation energies of Be, BH and CH$_2$ (dots, we exclude nitroxyl because of its strong correlations) as a function of $f_l \leq 1$. However, we are interested in the contribution to the double excitation gap, $E_{\text{c},S_2} - E_{\text{c},S_0} \approx \mathcal{E}_\text{c}^{\text{RPA}}(f_l = 2) - \mathcal{E}_\text{c}^{\text{RPA}}(f_l = 0)$, which requires extending results to $f_l = 2$ – here done by fitting and extrapolating. A linear fit (shown in
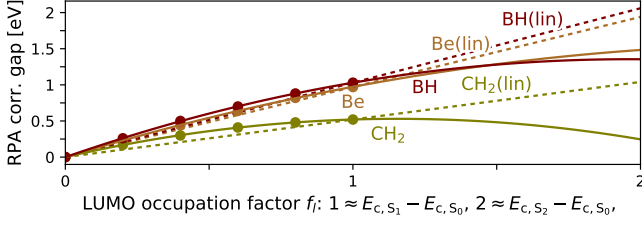
FIG. 2. RPA correlation energy gap, $\mathcal{E}_c^{\mathrm{RPA}}(f_l) - \mathcal{E}_c^{\mathrm{RPA}}(0)$, [eV] versus f_l for Be, BH and CH_2. Computed values are shown as dots while lines show extrapolated values using the same relationship as exchange (dashed purple, Be; navy, BH; and green, CH_2); and via a quadratic fit (solid red/blue/teal).

the figure) between $f_l = 0$ and $f_l = 1$ yields, $E_{c,S_2} = 2E_{c,S_1} - E_{c,S_0}$, which we recognise as the correlation energy contribution from eq. (6). However, it also reveals substantial curvature in the computed ($0 \leq f_l \leq 1$) values. We thus also show a quadratic fit, the simplest model that can capture the curvature, to better extend results to $f_l = 2$. Self-interaction errors and lack of density-driven correlations [23–25] mean RPA correlation gaps are not quantitative. Nonetheless, we do expect RPA to offer useful qualitative insights into the structure of $\mathcal{E}_c$ as weights are varied, e.g., as $w_{S_2} \to 1$ ($f_l \to 2$).

The most important revelation of the figure is that the $f_l = 2$ correlation energy from the (more accurate) quadratic extrapolation is significantly lower than the linear fit in all cases. We therefore expect that at least some of the over-estimation of correlation energies comes from *assuming* [in eq. (6)] that an exact relationship [eq. (5)] for exchange also applies to correlations, whereas the *RPA reveals it does not*. That is,

$$E_{c,S_1}^{\mathrm{DFA}} \approx E_{c,T_0}^{\mathrm{DFA}} , \qquad E_{c,S_2}^{\mathrm{DFA}} \not\approx 2E_{c,T_0}^{\mathrm{DFA}} - E_{c,S_0}^{\mathrm{DFA}} , \qquad (9)$$

where $\approx$ indicates that any additional ensemble errors are likely to be similar in magnitude to typical DFA errors, whereas $\not\approx$ indicates that they are likely to be larger.

To improve approximations for correlation energies, we exploit this insight from the RPA. To begin, let us consider a formal device which was used by Becke, Savin and Stoll (BSS) [46] to generate a local density approximation (LDA) that could preserve the degeneracy of multiplets. They replaced the spin polarization, $\zeta = \frac{|n_\uparrow - n_\downarrow|}{n}$, in the regular spin-dependent LDA by a function of the on-top (ot) pair density $\zeta \to \zeta^{\mathrm{ot}}$ (more below) in an otherwise spinless (restricted) theory. Specifically, they used the exact relationship, $\zeta = \zeta^{\mathrm{ot}} := \sqrt{1 - 2P_{\mathrm{Hx}}/n^2}$, for a single Slater determinant, where P_{Hx} is the KS on-top pair density. This result was elegantly further justified in Ref. 47 as a consistent way to escape the symmetry dilemma in spin-unrestricted DFT calculations. Crucially, we show that ζ^{ot} can also be exploited to mimic the *correction* which is required to improve RPA-inspired correlation energies for double excitations.

Next, let us tailor the BSS replacement for ensembles: i) use $P_{\mathrm{Hx},S_0}^{\mathrm{FDT}} = n_{S_0}^2 + P_{x,S_0}^{\mathrm{FDT}}$ in ground states to rewrite $\zeta^{\mathrm{ot}} = [-2P_x^{\mathrm{FDT}}/n^2 - 1]^{1/2}$ for general states; ii) write eq. (2) as $\int n_{2,x}^{\mathrm{FDT}}(\boldsymbol{r}, \boldsymbol{r}') \frac{d\boldsymbol{r} d\boldsymbol{r}'}{2|\boldsymbol{r} - \boldsymbol{r}'|}$ to obtain $-P_x^{\mathrm{FDT}}(\boldsymbol{r}) = -n_{2,x}^{\mathrm{FDT}}(\boldsymbol{r}, \boldsymbol{r}) = \sum_{ij} f_{\max(i,j)} n_i(\boldsymbol{r}) n_j(\boldsymbol{r})$ where $n_i = |\phi_i|^2$ is the density of orbital, i; iii) obtain,

$$\zeta^{\mathrm{ot}}(\boldsymbol{r}) = \frac{\left[\sum_{ij} (2f_{\max(i,j)} - f_i f_j) n_i(\boldsymbol{r}) n_j(\boldsymbol{r}) \right]^{\frac{1}{2}}}{\sum_i f_i n_i(\boldsymbol{r})} . \qquad (10)$$

By inspection, one sees that (10) reproduces the usual results for non-degenerate ground states, ($\zeta^{\mathrm{ot}} = 0$) doublets ($\zeta_{D_0}^{\mathrm{ot}} = \frac{n_h}{n}$) and single excitation/triplets ($\zeta_{S_1}^{\mathrm{ot}} = \zeta_{T_0}^{\mathrm{ot}} = \frac{n_h + n_l}{n}$). Thus, eq. (10) gives "out of the box" DFA results for singular, doublet and triplet ground states. Importantly, and unlike other formulae that are equivalent in ground states, $f_i \leq 2$ ensures that eq. (10) is always real so does not require further adjustment to accommodate negative values in the square root, e.g. eq. (11) of Ref. 48.
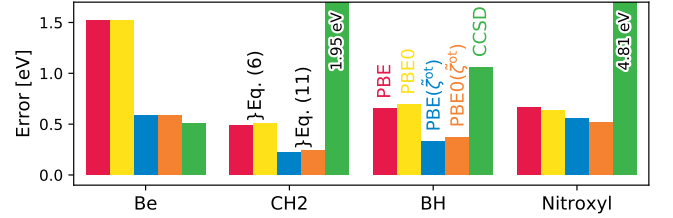

FIG. 3. PBE and PBE0 errors in double excitation energies using eq. (6) (red and yellow, respectively) and eq. (11) (blue and orange). EOM-CCSD (green) results are also included for reference – numbers indicate "off-graph" values.

An additional complication arises in the case of a double excitation between non-degenerate HOMO and LUMO. For regions where the "core" orbital densities are small ($n_{c<h} \ll n_h, n_l$) we obtain, $\zeta_{S_2}^{\mathrm{ot}} \approx \sqrt{2n_h/n_l}$, by using $f_h = 0$ and $f_l = 2$ for the double excitation. When $n_h(\boldsymbol{r}) \approx n_l(\boldsymbol{r})$ this yields a value of $\zeta^{\mathrm{ot}} \approx \sqrt{2} > 1$. A degenerate LUMO can also yield $\zeta^{\mathrm{ot}} > 1$ in single excitations. As a final step toward utilizing eq. (10) in approximations we therefore need a way to extend existing DFA to $\zeta > 1$. One formula that achieves this is,

$$\mathcal{E}_{\mathrm{Hxc}}^{(\tilde{\zeta}^{\mathrm{ot}})} := \mathcal{E}_{\mathrm{Hx}}^{\mathrm{DFA}} + \sum_{k=0}^{2} w_{S_k} E_{c,S_k}^{\mathrm{DFA}(\tilde{\zeta}^{\mathrm{ot}})} , \qquad (11)$$

where $E_{c,S_k}^{\mathrm{DFA}(\tilde{\zeta}^{\mathrm{ot}})} := \int d\boldsymbol{r} \, n_s^{S_k S_k} \epsilon_c^{\mathrm{DFA}}(n_s^{S_k S_k}, \nabla n_s^{S_k S_k}, \tilde{\zeta}_{S_k}^{\mathrm{ot}})$ uses an heuristic model $\tilde{\zeta}^{\mathrm{ot}} := \min(\zeta^{\mathrm{ot}}, [\zeta^{\mathrm{ot}}]^{-1}) \leq 1$ for the effective polarization. Eq. (11) is constructed to reproduce "out of the box" DFA energies for ground states ($\zeta^{\mathrm{ot}} = \tilde{\zeta}^{\mathrm{ot}} \leq 1$). Crucially, it also mimics the downward curvature of RPA correlation energies for $f_l \to 2$ ($\zeta^{\mathrm{ot}} > 1$, $\tilde{\zeta}^{\mathrm{ot}} < 1$) and thus ensures that correlation energies for double excitations become more like $\zeta \to 0$.

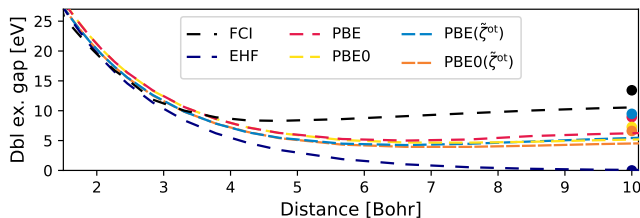FIG. 4. Double excitation gap for H_2 using FCI (black), HF (Navy), PBE (red), PBE0 (yellow), PBE($\tilde{\zeta}^{ot}$) (blue) and PBE0($\tilde{\zeta}^{ot}$) (orange). Dots show the dissociation gap.

Figure 3 compares results using eq. (11) against results using eq. (6). We see that the new formula – denoted DFA($\tilde{\zeta}^{ot}$) – substantially improves on eq. (6) in all cases. Except for Be, eq. (11) also out-performs equation-of-motion (EOM) coupled-cluster singles/doubles (CCSD) calculations [49] – significantly so in CH_2 and nitroxyl. We thus see that an improved model of correlations fixes the most egregious failures of ensemblized DFT and produces reasonable results. Technical details in SM-V.

Before concluding, we briefly address the prototypical "difficult case" of double excitations in dissociating H_2. [8–10, 50–52] Figure 4 compares dissociation curves computed using EDFT against exact FCI calculations. It reveals that, like the H_2 ground state [24] and despite strong correlations, both PBE and PBE($\tilde{\zeta}^{ot}$) reproduce the correct $-1/D$ asymptotic behaviour, albeit with an underestimated limit. Full details in SM-VI.

In conclusion, we presented a formal and practical ensemble density functional approach to double excitations. First, we showed that a rigorous exact exchange energy expression for double excitations is equivalent to that of two triplets minus a singlet [eq. (5)] – this counter-intuitive result enables practical reuse of standard exchange-only DFAs. In a second, non-trivial step, we then showed that the corresponding correlation requires additional sophistications. Guided by first principles, we developed an ensemble extension of the RPA expression, which inspired a practical approximation based on the on-top pair-density [eq. (11)] – thus overcoming a natural yet inconsistent guess [eq. (6)].

Results using the EDFAs developed here are already useful for the difficult and varied double excitations studied. Future work should improve our understanding of how on-top pair-densities affect correlations, so that we can devise even better ways to ensemblize conventional DFAs and deal with excited state correlations. Tests should also be extended to larger systems.

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[29] Specifically, minimization is over ensembles, $\hat{\Gamma}_{\boldsymbol{w}}$, with weights, $\boldsymbol{w}$, yielding the target density, $\text{Tr}[\hat{\Gamma}_{\boldsymbol{w}}\hat{n}] = n$.

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