

## Double excitations in molecules from ensemble density functionals: Theory and approximations

Tim Gould<sup>1,\*</sup>, Leeor Kronik<sup>2</sup>, and Stefano Pittalis<sup>3</sup>

<sup>1</sup>Queensland Micro- and Nanotechnology Centre, Griffith University, Nathan, Queensland 4111, Australia

<sup>2</sup>Department of Molecular Chemistry and Materials Science, Weizmann Institute of Science, Rehovoth 7610000, Israel

<sup>3</sup>CNR-Istituto Nanoscienze, Via Campi 213A, I-41125 Modena, Italy



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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 [Gould *et al.*, *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. In passing, to analyze correlation, we extend the random-phase approximation to ensembles. We then show, using selected test systems, that standard DFT approximations may be adapted to tackle double excitations based on theoretically motivated simple formulas that employ ensemble extensions of expressions that use the on-top pair density.

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### I. INTRODUCTION

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 to both 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 nontrivial 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 in model double excitations [14–17] and as a useful framework for wave-function-based methodologies [18–21].

In this paper, we employ recent theory advances concerning the structure of exact ensemble functionals [22–26] with the goal of building a high-quality general-purpose ensemble DFA (EDFA) that can predict double-excitation energies. First, we show that exact ensemble exchange (“x”) expressions acquire unexpected forms on double excitations. Importantly, our analysis reveals that exchange can be tackled via straightforward reuse of standard DFAs. Second, we extend the random-phase approximation (RPA) to ensembles to scrutinize limitations of existing correlation (“c”) DFAs and to provide a strategy to reuse them. Third, 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. Last, we demonstrate that EDFAs based on these results are competitive against prominent wave-function-based alternatives.

### II. ENSEMBLE DENSITY-FUNCTIONAL THEORY

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  $|S_2\rangle$  [27]. 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  $\mathcal{E}[v] = \min_{\hat{\Gamma}} \text{Tr}[\hat{\Gamma}(\hat{T} + \hat{W} + \hat{v})] = w_{S_0}E_{S_0} + w_{S_1}E_{S_1} + w_{S_2}E_{S_2}$  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  $\hat{v} = \int v(\mathbf{r})\hat{n}(\mathbf{r})d\mathbf{r}$  is the external-potential operator defined using the density operator  $\hat{n}$ . Note that Eq. (1) easily generalizes to ensembles mixing degenerate

\*t.gould@griffith.edu.au

states, where an essential general condition is to work with *totally* symmetric ensembles [28]. Note further that single- and double-excitation energies of the system can be computed by varying the weights, e.g.,  $E_{S_2} = \partial_{w_{S_2}} \mathcal{E}$ .

We may equivalently write, analogous to conventional DFT,

$$\mathcal{E}[n] = \mathcal{T}_s[n] + \mathcal{E}_{\text{HX}}[n] + \mathcal{E}_c[n] + \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r}, \quad (2)$$

where  $\mathcal{T}_s$ ,  $\mathcal{E}_{\text{HX}}$ , and  $\mathcal{E}_c$  are the ensemble Kohn-Sham (KS) kinetic-energy, Hartree-exchange (“HX”), and correlation density functionals, respectively. Note the dependence of the functional on the ensemble weights is implicit in the use of the calligraphic letters. In the following we further shorten our notation by dropping the obvious dependence on the ensemble particle density  $n$ .

As usual, the KS potential is given by

$$v_s(\mathbf{r}) \equiv v(\mathbf{r}) + \frac{\delta \mathcal{E}_{\text{HX}}}{\delta n(\mathbf{r})} + \frac{\delta \mathcal{E}_c}{\delta n(\mathbf{r})}. \quad (3)$$

Because we work with totally symmetric ensembles,  $v_s$  (Eq. (3) or generalizations [29]) has the *same* symmetry as the external potential  $v$ . Thus, the corresponding single-particle states are not only automatically orthogonal to each other but also symmetry adapted [28].

Our goal in this work is to devise DFAs for  $\mathcal{E}_{\text{HX}}$  and  $\mathcal{E}_c$  that are accurate for double excitations. To this end, let us first recall the ansatz-free definitions of these functionals [23]:  $\mathcal{T}_s = \mathcal{F}^0$ ,  $\mathcal{E}_{\text{HX}} = \lim_{\lambda \rightarrow 0^+} \frac{\mathcal{F}^\lambda - \mathcal{T}_s}{\lambda}$ , and  $\mathcal{E}_c = \mathcal{F}^1 - \mathcal{T}_s - \mathcal{E}_{\text{HX}}$  [24]. Here, we introduced the universal functional  $\mathcal{F}^\lambda[n] = \min_{\hat{w} \rightarrow n} \text{Tr}[\hat{\Gamma}_w(\hat{T} + \lambda \hat{W})]$ , which adiabatically connects the noninteracting ( $\lambda = 0$ ,  $|S_{s,k}\rangle$ ) and interacting ( $\lambda = 1$ ,  $|S_k\rangle$ ) limits [30].

A major advantage of EDFT over DFT is that the ensemble KS states are *noninteracting* configuration-state functions (CSFs) rather than single Slater determinants [23], i.e., *minimal* linear combinations of Slater determinants which are symmetry adapted with respect to both spin and spatial degrees of freedom [31]. Thus, interacting and KS states can be labeled by the same quantum numbers. For our initial example [see Eq. (1)] we obtain

$$\hat{\Gamma}_s = w_{S_0}|S_{s,0}\rangle\langle S_{s,0}| + w_{S_1}|S_{s,1}\rangle\langle S_{s,1}| + w_{S_2}|S_{s,2}\rangle\langle S_{s,2}|, \quad (4)$$

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,  $h \rightarrow l$ , from the highest occupied molecular orbital (HOMO)  $h$  to the lowest unoccupied molecular orbital (LUMO)  $l$ ; and  $|S_{s,2}\rangle := |[c^2]l^2\rangle$  as the double excitation on  $h \rightarrow l$ . Here,  $[c^2] \equiv 1^2 \dots (h-1)^2$ .

We stress that spin-restricted orbitals,  $\phi_{i\uparrow} = \phi_{i\downarrow}$ , are a direct consequence of preserving symmetries within the EDFT formalism [23,28]. They appear because Eq. (3) preserves both spatial and spin symmetries even in states (e.g., doublets or triplets) that are usually treated by unrestricted orbitals (UKS). One may say that a restricted KS (RKS) formalism is used throughout. But it is more appropriate to say that a symmetry-adapted KS formalism is used throughout.

In fact, the symmetry adaptation is even more comprehensive. Not only are the single-particle orbitals spin orbitals,

but the many-particle KS states  $|S_{s,k}\rangle$  are proper (multideterminant) spin eigenstates (singlets, triplets, etc). Symmetry adaptation is also useful to deal with the structure of the multiplets related to the spatial degrees of freedom: we use this feature later when we study Be and BH. Thus, the KS states  $|S_{s,k}\rangle$  have a transparent and direct spectroscopical meaning with well-defined quantum numbers and appropriate degeneracies. The employed symmetry-adapted formalism outperformed both UKS DFT and TDDFT in predicting single excitations [32]. In  $\text{O}_2$ , for example, the error in predicted triplet-singlet energy gaps using symmetry-adapted EDFT was reduced by a quarter from a similar UKS-based difference of self-consistent field ( $\Delta\text{SCF}$ ) calculation.

We then use Eq. (4) to obtain ensemble kinetic and Hartree-exchange energies [23],

$$\mathcal{T}_s = \text{Tr}[\hat{\Gamma}_s \hat{T}] = \sum_{k=0}^2 w_{S_k} \langle S_{s,k} | \hat{T} | S_{s,k} \rangle, \quad (5)$$

$$\mathcal{E}_{\text{HX}} = \text{Tr}[\hat{\Gamma}_s \hat{W}] = \sum_{k=0}^2 w_{S_k} \langle S_{s,k} | \hat{W} | S_{s,k} \rangle, \quad (6)$$

where both involve sums over the weighted contributions of KS-CSFs.  $\mathcal{E}_{\text{HX}}$  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 [33] sets  $E_{\text{HXC}}^{\text{PBE0}} := E_{\text{H}} + 0.25E_{\text{x}}^{\text{HF}} + 0.75E_{\text{x}}^{\text{PBE}} + E_{\text{c}}^{\text{PBE}} = E_{\text{HX}} + 0.75(E_{\text{x}}^{\text{PBE}} - E_{\text{x}}^{\text{HF}}) + E_{\text{c}}^{\text{PBE}}$  using Hartree-Fock (HF) exchange, with Perdew-Burke-Ernzerhof (PBE) [34] exchange and correlation DFA.

Recently, a fluctuation-dissipation theorem (FDT) was extended and used to further resolve  $\mathcal{E}_{\text{HX}} := \mathcal{E}_{\text{H}}^{\text{FDT}} + \mathcal{E}_{\text{x}}^{\text{FDT}}$  into “H” and “x” energy expressions that are compatible with existing DFAs [25]. The same extension also offers insights into correlations, discussed further below. The key arguments of Ref. [25] 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  $\chi$  of the ensemble; (iii) the KS response  $\chi_s$  allows us to define  $\mathcal{E}_{\text{x}}^{\text{FDT}}$  in a way which is formally consistent with existing “x”-DFA.  $\mathcal{E}_{\text{H}}^{\text{FDT}}$  then includes all the remaining CSF terms, while state-driven correlation [24] can be handled by relating the KS to the interacting response function.

### III. APPROXIMATIONS FOR EXCHANGE ENERGIES

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

$$\mathcal{E}_{\text{x}}^{\text{FDT}} := -\frac{1}{2} \sum_{ij} f_{\max(i,j)} (ij|ji) \quad (7)$$

for “x,” where the expression given above is a convenient corollary of a result from Ref. [25] that is derived in Appendix A. Here,  $f_i = \sum_k w_{S_k} \theta_i^{S_k}$  are the average occupations of the orbital  $\phi_i$ , 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.  $(ij|kl) := \int \frac{drdr'}{|r-r'|} \phi_i(\mathbf{r})\phi_j(\mathbf{r}')\phi_k(\mathbf{r})\phi_l(\mathbf{r}')$  and real-valued orbitals are used throughout this work.

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

$$\mathcal{E}_{\text{Hx}}^{\text{PBE0}} := \mathcal{E}_{\text{Hx}} + 0.75(\mathcal{E}_{\text{x}}^{\text{PBE}} - \mathcal{E}_{\text{x}}^{\text{FDT}}). \quad (8)$$

The details may, of course, be varied to cover other DFA, including range-separated hybrids. The next crucial step is to break  $\mathcal{E}_{\text{x}}^{\text{FDT}} := \sum_k w_k \mathcal{E}_{\text{x},S_k}^{\text{FDT}}$  into individual state contributions so that we can replace exact “x” expressions by *existing* “x”-DFA expressions. For this important task, we follow Fromager [26] to rigorously define

$$\mathcal{E}_{\text{x},S_k}^{\text{FDT}} := \frac{\partial \mathcal{E}_{\text{x}}^{\text{FDT}}}{\partial w_{S_k}} = -\frac{1}{2} \sum_{ij} \theta_{\max(i,j)}^{S_k} (ij|ji), \quad (9)$$

where we used  $f_{\max(i,j)} = \sum_k w_k \theta_{\max(i,j)}^{S_k}$  in Eq. (7) to derive the second expression. Note that applying the same principle to Eqs. (5) and (6) yields  $T_{S,S_k} = \langle S_{s,k} | \hat{T} | S_{s,k} \rangle = \sum_i f_i \int \frac{1}{2} |\nabla \phi_i|^2 d\mathbf{r}$  and  $E_{\text{Hx},S_k} = \langle S_{s,k} | \hat{W} | S_{s,k} \rangle$ , as expected. We expand on  $E_{\text{Hx},S_k}$  below, near Eq. (12).

It follows from (9) that  $\mathcal{E}_{\text{x},S_0}^{\text{FDT}} = -\sum_{i,j \in \{c,h\}} (ij|ji) \equiv \mathcal{E}_{\text{x},S_0}^{\text{HF}}$  adopts its conventional HF form for the ground state, by construction [25]. Further algebraic manipulation of the above equations (Appendix B) yields

$$E_{\text{x},S_1}^{\text{FDT}} = E_{\text{x},T_0}^{\text{HF}}, \quad E_{\text{x},S_2}^{\text{FDT}} = 2E_{\text{x},T_0}^{\text{HF}} - E_{\text{x},S_0}^{\text{HF}} \neq E_{\text{x},S_2}^{\text{HF}}, \quad (10)$$

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

Equation (10) 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 [32], 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 *two times a triplet minus a singlet*.

Finally, using Eq. (10) in Eq. (8) yields  $\mathcal{E}_{\text{Hx}}^{\text{DFA}} := \mathcal{E}_{\text{Hx}} + \bar{\alpha}[(w_{S_0} - w_{S_2})(E_{\text{x},S_0}^{\text{DFA}} - E_{\text{x},S_0}^{\text{HF}}) + (w_{S_1} + 2w_{S_2})(E_{\text{x},T_0}^{\text{DFA}} - E_{\text{x},T_0}^{\text{HF}})]$  for the “Hx” part of general hybrids (Appendix B), where  $\bar{\alpha} = 1 - \alpha$  is the complement to the Fock exchange fraction  $\alpha$ . The above analysis means we can *now reuse any existing*  $E_{\text{x},S_0/T_0}^{\text{DFA}}$  in  $\mathcal{E}_{\text{Hx}}^{\text{DFA}}$ . Previous work on single excitations successfully assumed [32] that  $E_{\text{c},S_k}^{\text{DFA}}$  and  $E_{\text{x},S_k}^{\text{DFA}}$  obey the same combination laws. If we extend this to double excitations, we

TABLE I. (Pair) coefficients for “x” and “Hx” with different degeneracies  $D_l$  of the LUMO. Here,  $f_h = 2w_{S_0} + w_{S_1}$ ,  $f_l = \frac{w_{S_1} + 2w_{S_2}}{D_l}$  are equal for all LUMO, and  $F_{lh} = F_{hl}$ . Note, “arb.” (arbitrary) means the result applies to any value of  $D_l$ .

State	$D_l$	Example	$f_h$	$f_l$	$F_{hh}^J$	$F_{hl}^J$	$F_{ll}^J$	$F_{hh}^K$	$F_{hl}^K$	$F_{ll}^K$
$S_0$	arb.	all molecules	2	0	4	0	0	-2	0	0
$S_1$	arb.	all molecules	1	$\frac{1}{D_l}$	1	$f_l$	$f_l$	-1	$f_l$	$-f_l$
$S_2$	1	CH <sub>2</sub>	0	2	0	0	4	0	0	-2
$S_2$	2	BH	0	1	0	0	$\frac{1}{2}$	0	0	0
$S_2$	3	Be	0	$\frac{2}{3}$	0	0	$\frac{1}{5}$	0	0	$\frac{1}{15}$

then obtain an “Hxc” functional,

$$\mathcal{E}_{\text{Hxc}}^{\text{DFA}} := \mathcal{E}_{\text{Hx}} + (w_{S_0} - w_{S_2})[\bar{\alpha}(E_{\text{x},S_0}^{\text{DFA}} - E_{\text{x},S_0}^{\text{HF}}) + E_{\text{c},S_0}^{\text{DFA}}] + (w_{S_1} + 2w_{S_2})[\bar{\alpha}(E_{\text{x},T_0}^{\text{DFA}} - E_{\text{x},T_0}^{\text{HF}}) + E_{\text{c},T_0}^{\text{DFA}}]. \quad (11)$$

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 ensembles that average over an equal mixture of all degenerate excited states, to yield densities and effective potentials that preserve fundamental spatial symmetries [28]. In general,

$$E_{\text{Hx},S_k} := \frac{1}{2} \sum_{ij} [F_{ij}^{J,S_k} (ij|ij) + F_{ij}^{K,S_k} (ij|ji)], \quad (12)$$

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 reported in Table I and derived in Appendix B.

Although Eq. (11) 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. [29] and because of errors introduced by density-driven correlations [24], 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 them to mixtures of only ground and doubly excited states [35], (ii) optimize orbitals (mostly) via minimization over unitary transformations [29], and (iii) use the extrapolation procedure described in Ref. [32] to approximately remove density-driven correlation errors [24]. Full details are given in Appendix C.

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 fivefold degenerate), CH<sub>2</sub>, BH (twofold degenerate), and nitroxyl (ONH). Reference data are from Ref. [1] (Be and nitroxyl) and full-configuration-interaction (FCI) results (CH<sub>2</sub> and BH) computed for this work. Energies are evaluated using Eq. (11) for PBE [34] (red,  $\alpha = 0$ ) and PBE0 [33] (yellow,  $\alpha = 0.25$ ). Gaps using the range-separated hybrid functional  $\omega\text{B97X}$  [36] (teal) and hybrid functional Becke three-parameter Lee-Yang-Parr (B3LYP; purple) [37] are of

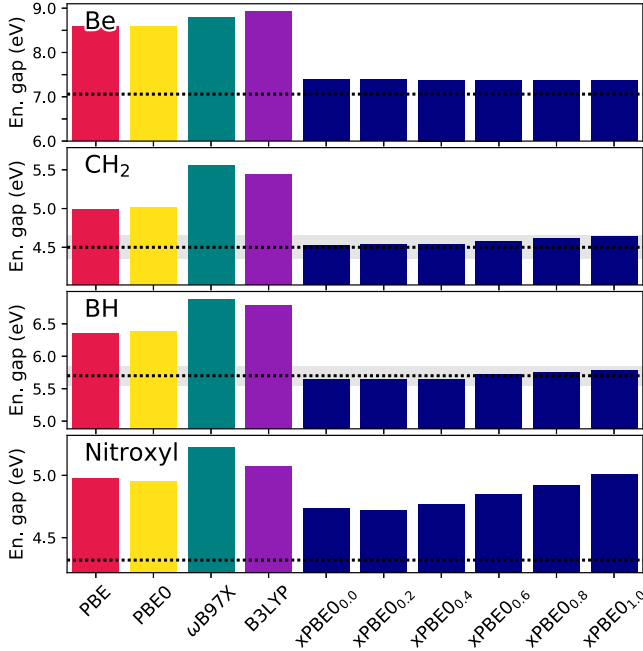


FIG. 1. Excitation energy gaps (in eV) for the double excitation of Be, CH<sub>2</sub>, BH, and nitroxyl computed using FDT-derived PBE energy expressions [using Eq. (11)] with (PBE, red; PBE0, yellow; ωB97x, teal; and B3LYP, purple) and without (xPBE<sub>α</sub>, navy) correlations included. The dotted line is the benchmark value, and the shaded gray area indicates error bars for BH and CH<sub>2</sub>.

slightly worse quality. Further technical details are given in Appendix C. Despite the rigorous theory behind the “Hx” components in Eq. (11), the results are uninspiring. This stands in contrast to the success of similar ensemble DFA in predicting triplet and single excitations [32].

To understand why energies are so poor we first perform “x”-only PBE0-like [labeled xPBE<sub>α</sub> and defined via Eq. (11) with  $E_c = 0$ , navy] calculations to investigate the contribution of exchange to the error. Two points are notable: (i) “x”-only FDT results depend only weakly on  $\alpha$ , and the variation is larger with stronger correlations, which suggests that exchange physics is treated correctly at the density-functional level. (ii) Ensemble HF theory (xPBE<sub>1</sub>) is rather accurate for Be, CH<sub>2</sub>, 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.

#### IV. APPROXIMATIONS FOR CORRELATION ENERGIES

As a natural next step, we seek to replicate the success of  $\mathcal{E}_x^{\text{FDT}}$  by using the FDT [38] to tackle  $\mathcal{E}_c$ . Exact evaluation is impossible in general, so we instead invoke the RPA [38–42] that has found widespread success in modeling difficult ground states [40–42] and in providing constraints for popular DFAs for correlation [43,44]. We ensemble the RPA by using the same KS *ensemble* density-density response

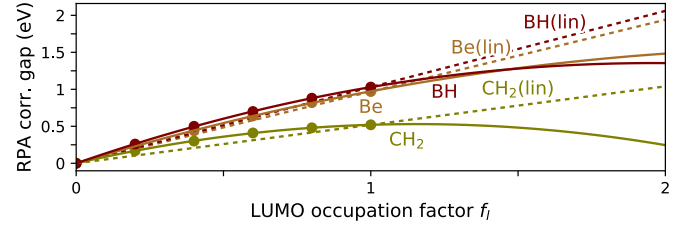


FIG. 2. RPA correlation-energy gap  $\mathcal{E}_c^{\text{RPA}}(f_l) - \mathcal{E}_c^{\text{RPA}}(0)$  (eV) versus  $f_l$  for Be, BH, and CH<sub>2</sub>. Computed values are shown as dots, while lines show extrapolated values using the same relationship as exchange (dashed lines: brown, Be; maroon, BH; and olive, CH<sub>2</sub>) and via a quadratic fit (solid lines).

function used to derive Eq. (7) [25],

$$\hat{\chi}_s(i\omega) = \sum_{ij} \frac{(f_i - f_j)(\epsilon_i - \epsilon_j)}{(\epsilon_i - \epsilon_j)^2 + \omega^2} \hat{\rho}_i \hat{\rho}_j, \quad (13)$$

$$\mathcal{E}_c^{\text{RPA}} := \int_0^\infty \frac{d\omega}{2\pi} \text{Tr}[\ln(1 - \hat{\chi}_s \hat{W}) + \hat{\chi}_s \hat{W}]. \quad (14)$$

Equation (14) thereby inherits an explicit dependence on the ensemble via the occupation factors  $\{f_i\}$ . Here,  $\epsilon_i$  is the KS eigenvalue of orbital  $i$ ; Tr and ln indicate operator trace and logarithm, and  $\text{Tr}[\hat{\rho}_i \hat{W} \hat{\rho}_j] = (ij|ji)$ . Using (13) in (14) 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 that  $f_l > 1$  leads to negative values in the logarithm). Details of RPA calculations are given in Appendix D.

Note that the frequency dependence in Eq. (14) 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<sub>2</sub> (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,  $E_{c,S_2} - E_{c,S_0} \approx \mathcal{E}_c^{\text{RPA}}(f_l = 2) - \mathcal{E}_c^{\text{RPA}}(f_l = 0)$ , which requires extending results to  $f_l = 2$ , here done by fitting and extrapolating. A linear fit (shown in Fig. 2) between  $f_l = 0$  and  $f_l = 1$  yields  $E_{c,S_2} = 2E_{c,S_1} - E_{c,S_0}$ , which we recognize as the correlation-energy contribution from Eq. (11). 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 also extend results to  $f_l = 2$ . Self-interaction errors [45–47] in the open-shell excitations 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  $w_{S_2} \rightarrow 1$  ( $f_l \rightarrow 2$ ).

The most important revelation of Fig. 2 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 overestimation of correlation energies comes from *assuming* [in Eq. (11)] that an exact relationship [Eq. (10)] for exchange also applies to

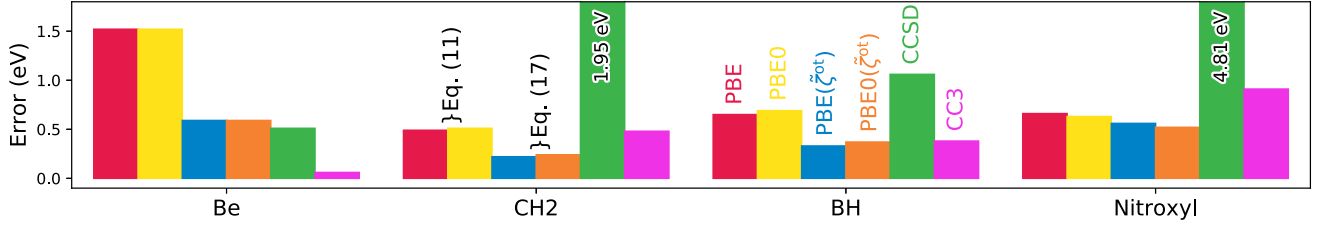


FIG. 3. PBE and PBE0 errors in double-excitation energies using Eq. (11) (red and yellow, respectively) and Eq. (17) (blue and orange). EOM-CCSD (green) and EOM-CC3 (magenta) results are also included for reference. Numbers indicate “off-graph” values.

correlations, whereas the RPA reveals *it does not*. That is,

$$E_{c,S_1}^{\text{DFA}} \approx E_{c,T_0}^{\text{DFA}}, \quad E_{c,S_2}^{\text{DFA}} \not\approx 2E_{c,T_0}^{\text{DFA}} - E_{c,S_0}^{\text{DFA}}, \quad (15)$$

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) [48] 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  $\zeta \rightarrow \zeta^{\text{ot}}$  (more below) in an otherwise spinless (restricted) theory. Specifically, they used the exact relationship  $\zeta = \zeta^{\text{ot}} := \sqrt{1 - 2P_{\text{Hx}}/n^2}$  for a single Slater determinant, where  $P_{\text{Hx}}$  is the KS on-top pair density. This result was elegantly further justified in Ref. [49] as a consistent way to escape the symmetry dilemma in spin-unrestricted DFT calculations. Crucially, we show that  $\zeta^{\text{ot}}$  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  $P_{\text{Hx},S_0}^{\text{FDT}} = n_{S_0}^2 + P_{x,S_0}^{\text{FDT}}$  in ground states to rewrite  $\zeta^{\text{ot}} = [-2P_x^{\text{FDT}}/n^2 - 1]^{1/2}$  for general states, (ii) write Eq. (7) as  $\int n_{2,x}^{\text{FDT}}(\mathbf{r}, \mathbf{r}') \frac{d\mathbf{r}d\mathbf{r}'}{2|\mathbf{r}-\mathbf{r}'|}$  to obtain  $-P_x^{\text{FDT}}(\mathbf{r}) = -n_{2,x}^{\text{FDT}}(\mathbf{r}, \mathbf{r}) = \sum_{ij} f_{\max(i,j)} n_i(\mathbf{r}) n_j(\mathbf{r})$ , where  $n_i = |\phi_i|^2$  is the density of orbital  $i$ , and (iii) obtain

$$\zeta^{\text{ot}}(\mathbf{r}) = \frac{[\sum_{ij} (2f_{\max(i,j)} - f_i f_j) n_i(\mathbf{r}) n_j(\mathbf{r})]^{1/2}}{\sum_i f_i n_i(\mathbf{r})}. \quad (16)$$

By inspection, one sees that (16) reproduces the usual results for nondegenerate ground states ( $\zeta^{\text{ot}} = 0$ ), doublets ( $\zeta_{D_0}^{\text{ot}} = \frac{n_h}{n}$ ), and single excitations and triplets ( $\zeta_{S_1}^{\text{ot}} = \zeta_0^{\text{ot}} = \frac{n_h + n_l}{n}$ ). Thus, Eq. (16) gives “out-of-the-box” DFA results for singular, doublet, and triplet ground states. Importantly, unlike other formulas that are equivalent in ground states,  $f_i \leq 2$  ensures that Eq. (16) is always real and so does not require further adjustment to accommodate negative values in the square root, e.g., Eq. (11) of Ref. [50].

An additional complication arises in the case of a double excitation between nondegenerate HOMOs and LUMOs. For regions where the “core” orbital densities are small ( $n_{c<h} \ll n_h, n_l$ ) we obtain  $\zeta_{S_1}^{\text{ot}} \approx \sqrt{2n_h/n_l}$  by using  $f_h = 0$  and  $f_l = 2$  for the double excitation. When  $n_h(\mathbf{r}) \approx n_l(\mathbf{r})$ , this yields a

value of  $\zeta^{\text{ot}} \approx \sqrt{2} > 1$ . A degenerate LUMO can also yield  $\zeta^{\text{ot}} > 1$  in single excitations. As a final step toward utilizing Eq. (16) in approximations we therefore need a way to extend existing DFA to  $\zeta > 1$ . One formula that achieves this is

$$\mathcal{E}_{\text{Hxc}}^{(\zeta^{\text{ot}})} := \mathcal{E}_{\text{Hxc}}^{\text{DFA}} + \sum_{k=0}^2 w_{S_k} E_{c,S_k}^{\text{DFA}(\zeta^{\text{ot}})}, \quad (17)$$

where  $E_{c,S_k}^{\text{DFA}(\zeta^{\text{ot}})} := \int d\mathbf{r} n_s^{S_k} \epsilon_c^{\text{DFA}}(n_s^{S_k}, \nabla n_s^{S_k}, \zeta_{S_k}^{\text{ot}})$  uses a heuristic model  $\tilde{\zeta}^{\text{ot}} := \min(\zeta^{\text{ot}}, [\zeta^{\text{ot}}]^{-1}) \leq 1$  for the effective polarization. Equation (17) is constructed to reproduce out-of-the-box DFA energies for ground states ( $\zeta^{\text{ot}} = \tilde{\zeta}^{\text{ot}} \leq 1$ ). Crucially, it also mimics the downward curvature of RPA correlation energies for  $f_l \rightarrow 2$  ( $\zeta^{\text{ot}} > 1$ ,  $\tilde{\zeta}^{\text{ot}} < 1$ ) and thus ensures that correlation energies for double excitations become more like  $\zeta \rightarrow 0$ .

Figure 3 compares results using Eq. (17) against results using Eq. (11). We see that the new formula, denoted DFA( $\tilde{\zeta}^{\text{ot}}$ ), substantially improves on Eq. (11) in all cases. Except for Be, Eq. (17) also outperforms both equation-of-motion (EOM) coupled-cluster with single and double excitations (CCSD) calculations [51] and CC3 [52]. Thus, the improved model of correlations fixes the most egregious failures of ensembled DFT and produces reasonable results. Technical details are given in Appendix E.

Before concluding, we briefly address the prototypical “difficult case” of double excitations in dissociating  $\text{H}_2$  [8–10, 53–55]. Specifically, we study the transition formed by double promotion of the lowest  $\sigma$  orbital to the first unoccupied  $\sigma$  orbital. These two orbitals are a gerade-ungerade pair:  $\phi_{\sigma_g} \rightarrow \frac{1}{\sqrt{2}}[\phi_{1s,L} + \phi_{1s,R}]$  and  $\phi_{\sigma_u} \rightarrow \frac{1}{\sqrt{2}}[\phi_{1s,L} - \phi_{1s,R}]$ , where  $\rightarrow$  indicates the dissociation (large distance,  $D \rightarrow \infty$ ) limit and  $\phi_{1s,L}$  and  $\phi_{1s,R}$  indicate  $1s$  orbitals on the left and right H atoms. Analytic expressions may be obtained for large  $D$  and yield a double-excitation gap energy of  $\frac{1}{2} - 1/D$  Ha. The dissociation ( $D \rightarrow \infty$ ) gap is thus 13.6 eV.

Figure 4 compares dissociation curves for  $\sigma$  states computed using EDFT against exact FCI calculations. It reveals that, like the  $\text{H}_2$  ground state [25] and despite strong correlations, both PBE and PBE( $\tilde{\zeta}^{\text{ot}}$ ) reproduce the correct  $-1/D$  asymptotic behavior, albeit with an underestimated limit. Inclusion of FDT exchange in PBE0 worsens results by reducing both the effective charge and the asymptotic gap. Ensemble Hartree-Fock theory is even worse, predicting a zero gap for  $D \rightarrow \infty$ . Full details are given in Appendix F.

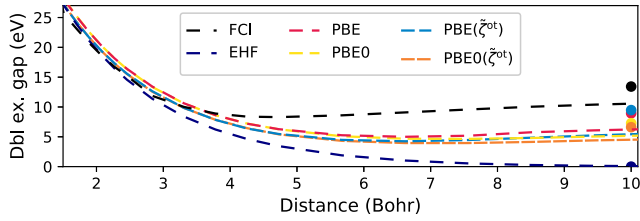


FIG. 4.  $H_2 \sigma_g \rightarrow \sigma_u$  double-excitation gap using FCI (black), HF (navy), PBE (red), PBE0 (yellow), PBE( $\zeta^{\text{ot}}$ ) (blue), and PBE0( $\zeta^{\text{ot}}$ ) (orange). Dots show the dissociation gap.

## V. CONCLUSIONS

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. (10)]; this counterintuitive result enables practical reuse of standard exchange-only DFAs. In a second, nontrivial step, we then showed that the corresponding correlation requires additional sophistication. 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. (17)], thus overcoming a natural yet inconsistent guess [Eq. (11)].

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 ensemble conventional DFAs and deal with excited-state correlations. Tests should also be extended to larger systems.

Our results do not apply directly to the solid state due to complexities in their ensemble treatment. They also do not apply directly to systems that are subject to an applied magnetic field or spin-orbit interactions. But the combination formula follows directly from foundational theories (variational principles [23,24,26], group properties [28], and fluctuation-dissipation theorems [25]), which may be extended to a larger class of systems. A first step toward solving these problems would be to derive the necessary analogs of the Gross-Oliveira-Kohn theorems [11,12].

## ACKNOWLEDGMENTS

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## APPENDIX A: DENSITY-DENSITY RESPONSE AND EXCHANGE FORMULAS

Before beginning the technical analysis, let us revise some of the key features of ensemble density-functional theory (EDFT). As with regular Kohn-Sham (KS) density-functional theory (DFT), EDFT uses the ensemble density as the fundamental variable. But again, as in regular DFT, the key ensemble density functionals  $\mathcal{T}_s[n]$  and  $\mathcal{E}_{\text{Hx}}[n]$  are orbital functionals that are implicit functionals of the density and

whose form depends explicitly on a set of orbitals  $\{\phi_i\}$  and on the states that are included in the ensemble.  $\mathcal{T}_s[n]$  is minimized for orbitals obeying the ensemble KS equations,

$$\left\{ -\frac{1}{2}\nabla^2 + v_s[n](\mathbf{r}) \right\} \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \quad (\text{A1})$$

which serve the same role as in conventional pure-state DFT and which implicitly define the effective KS potential  $v_s$  via the minimization. Here and throughout, we shall assume the orbitals are real and proscribed for mathematical convenience.

At this level, the key difference between EDFT and pure-state DFT is that the KS states  $|\Phi_{s,k}\rangle$  are not necessarily single Slater determinants but can be configuration-state functions (CSFs) formed on small sets of Slater determinants that are degenerate on the KS Hamiltonian,  $\hat{H}^{\lambda=0} = \hat{T} + \int n(\mathbf{r})\hat{v}_s(\mathbf{r})d\mathbf{r}$ . Whether it is a single Slater determinant or a CSF, each of these KS states has well-defined occupation factors  $\theta_i^{\Phi_{s,k}}$ , so that its density is  $n^{\Phi_{s,k}} = \langle \Phi_{s,k} | \hat{n} | \Phi_{s,k} \rangle = \sum_i \theta_i^{\Phi_{s,k}} |\phi_i|^2$ . The ensemble density  $n = \text{Tr}[\hat{\Gamma}_s \hat{n}]$ , with  $\hat{\Gamma}_s = \sum_k w_k |\Phi_{s,k}\rangle \langle \Phi_{s,k}|$ , is then

$$n(\mathbf{r}) = \sum_k w_k n^{\Phi_{s,k}} = \sum_k w_k \sum_i \theta_i^{\Phi_{s,k}} \phi_i^2 := \sum_i f_i \phi_i^2, \quad (\text{A2})$$

where  $f_i = \sum_k w_k \theta_i^{\Phi_{s,k}}$  is the average occupation factor of orbital  $\phi_i$ .

Therefore, the density of the system is determined uniquely by  $v_s$  and  $f_i$ . The average occupation factors  $f_i$  are determined uniquely by the form of the ensemble. In the nondegenerate case  $\hat{\Gamma}_s = w_{S_0} |S_{s,0}\rangle \langle S_{s,0}| + w_{S_1} |S_{s,1}\rangle \langle S_{s,1}| + w_{S_2} |S_{s,2}\rangle \langle S_{s,2}|$ , considered in the main text, we have

$$f_{i<h} = 2, \quad f_h = 2w_{S_0} + w_{S_1}, \quad f_l = w_{S_1} + 2w_{S_2}, \quad f_{i>l} = 0, \quad (\text{A3})$$

which we can find by recognizing the (i) all considered states have doubly occupied ‘‘core’’ ( $i < h$ ) orbitals, (ii) the ground state  $|S_{s,0}\rangle$  (with weight  $w_{S_0}$ ) has two electrons in the highest occupied molecular orbital (HOMO)  $h$  and none in the lowest unoccupied molecular orbital (LUMO)  $l$ , (iii) the single excitation  $|S_{s,1}\rangle$  ( $w_{S_1}$ ) has one HOMO and one LUMO, and (iv) the double excitation  $|S_{s,2}\rangle$  ( $w_{S_2}$ ) has two LUMOs and no HOMOs. Taking the weighted average gives Eq. (A3). We shall now restrict ourselves to this type of ensemble or, where appropriate, generalizations that are required by degeneracies.

The ensemble ‘‘Hx’’ energy is defined as

$$\mathcal{E}_{\text{Hx}} = \text{Tr}[\hat{\Gamma}_s \hat{W}] = \sum_k w_{S_k} \langle S_{s,k} | \hat{W} | S_{s,k} \rangle, \quad (\text{A4})$$

which formally [23] determines the valid CSFs used in the density but does not change the occupation factors  $f_i$ . Next, using the fluctuation-dissipation theorem extended to passive states, we can split ‘‘Hx’’ into an ‘‘H’’ and an ‘‘x’’ [25]. ‘‘H’’ has the compact form

$$\mathcal{E}_{\text{H}}^{\text{FDT}} = \sum_{kk'} \min(w_{S_k}, w_{S_{k'}}) \int \frac{d\mathbf{r}d\mathbf{r}'}{2|\mathbf{r}-\mathbf{r}'|} \times \langle S_{s,k} | \hat{n}(\mathbf{r}) | S_{s,k'} \rangle \langle S_{s,k'} | \hat{n}(\mathbf{r}') | S_{s,k} \rangle \quad (\text{A5})$$

but may be more conveniently defined as the difference of ‘‘Hx’’ and ‘‘x.’’ Therefore, here, we summarize and revisit the expression for only the ‘‘x’’ functional.

Equation (11) of Ref. [25] defines

$$\mathcal{E}_x^{\text{FDT}} := - \int \frac{d\mathbf{r}d\mathbf{r}'}{2|\mathbf{r}-\mathbf{r}'|} \left[ \int \chi_s(\mathbf{r}, \mathbf{r}'; i\omega) \frac{d\omega}{\pi} + n(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') \right], \quad (\text{A6})$$

so we see that the “x” functional depends on the ensemble density-density response  $\chi_s$  of a Kohn-Sham system with density  $n(\mathbf{r}) = \sum_i f_i |\phi_i(\mathbf{r})|^2$ . The response may be written as

$$\chi_s(\mathbf{r}, \mathbf{r}'; i\omega) := 2\text{Re} \sum_i f_i \phi_i^*(\mathbf{r}) G_i(\mathbf{r}, \mathbf{r}'; i\omega) \phi_i(\mathbf{r}') \quad (\text{A7})$$

in terms of the Green’s function,

$$G_i(\mathbf{r}, \mathbf{r}') = \sum_j \frac{\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')}{(\epsilon_i - \epsilon_j) + i\omega}, \quad (\text{A8})$$

obeying  $\{-\frac{1}{2}\nabla^2 + v_s(\mathbf{r}) + \epsilon - i\omega\}G_i(\mathbf{r}, \mathbf{r}'; i\omega) = \delta(\mathbf{r}-\mathbf{r}')$ .

We may, without loss of generality, assume real orbitals  $\phi_i$  to obtain

$$\begin{aligned} \chi_s &= \sum_{ij} 2f_i \rho_i(\mathbf{r}, \mathbf{r}') \rho_j(\mathbf{r}', \mathbf{r}) \frac{(\epsilon_i - \epsilon_j)}{(\epsilon_i - \epsilon_j)^2 + \omega^2} \\ &= \sum_{ij} (f_i - f_j) \frac{(\epsilon_i - \epsilon_j)}{(\epsilon_i - \epsilon_j)^2 + \omega^2} \rho_i(\mathbf{r}, \mathbf{r}') \rho_j(\mathbf{r}', \mathbf{r}), \end{aligned} \quad (\text{A9})$$

which is equivalent to Eq. (7) of the main text; the second expression comes from writing  $2 \sum_{ij} X_{ij} = \sum_{ij} (X_{ij} + X_{ji})$  and using  $\rho_i(\mathbf{r}, \mathbf{r}') := \phi_i(\mathbf{r})\phi_i(\mathbf{r}')$ . We can use (A9) in (A6) to write

$$\begin{aligned} \mathcal{E}_x^{\text{FDT}} &= - \sum_{ij} \int_{0^-}^{\infty} \frac{(f_i - f_j)(\epsilon_i - \epsilon_j)}{(\epsilon_i - \epsilon_j)^2 + \omega^2} \frac{d\omega}{2\pi} (ij|ji) \\ &\quad - \int n(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') \frac{d\mathbf{r}d\mathbf{r}'}{2|\mathbf{r}-\mathbf{r}'|}, \end{aligned} \quad (\text{A10})$$

where  $(ij|kl) := \int \phi_i(\mathbf{r})\phi_j(\mathbf{r}')\phi_k(\mathbf{r})\phi_l(\mathbf{r}') \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}$ , as in the main text.

Next, note that  $\int_{0^-}^{\infty} \frac{d\omega}{\pi} \frac{\Omega}{\Omega^2 + \omega^2} = \frac{1}{2} \text{sgn}(\Omega)$ , where  $\text{sgn}(\Omega) = \{-1, \Omega < 0; 0, \Omega = 0; 1, \Omega > 0\}$  is a sign function. Then,

$$\begin{aligned} \mathcal{E}_x^{\text{FDT}} &:= - \sum_{ij} (f_i - f_j) \frac{\text{sgn}(\epsilon_i - \epsilon_j)}{2} \frac{(ij|ji)}{2} \\ &\quad - \sum_{ij} \frac{f_i + f_j}{2} \frac{(ij|ji)}{2}, \end{aligned} \quad (\text{A11})$$

where we also used completeness of the orbitals to obtain  $\delta(\mathbf{r}-\mathbf{r}') = \sum_j \rho_j(\mathbf{r}, \mathbf{r}')$ , which we used to write  $\frac{1}{2}n(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') = \frac{1}{2} \sum_{ij} f_i \rho_i(\mathbf{r}, \mathbf{r}') \rho_j(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \sum_{ij} f_j \rho_i(\mathbf{r}, \mathbf{r}') \rho_j(\mathbf{r}, \mathbf{r}')$ .

Last, we can assume a nondegenerate ordered system ( $\epsilon_i > \epsilon_j$  for  $i > j$ ) to write  $\text{sgn}(\epsilon_i - \epsilon_j) = \text{sgn}(i - j)$ . Then,

$$\begin{aligned} \mathcal{E}_x^{\text{FDT}} &= - \frac{1}{2} \sum_{ij} \left[ \frac{f_i - f_j}{2} \text{sgn}(i - j) + \frac{f_i + f_j}{2} \right] (ij|ji) \\ &= - \frac{1}{2} \sum_{ij} f_{\max(i,j)} (ij|ji). \end{aligned} \quad (\text{A12})$$

We finally note that any equiensemble over degenerate states also obeys Eq. (A12) because  $f_i = f_j$  when  $\epsilon_i = \epsilon_j$ . Thus, the above result also applies to equiensembles.

## APPENDIX B: EXPRESSIONS FOR NONDEGENERATE AND DEGENERATE DOUBLE EXCITATIONS

Before beginning, we note that all discussion in this Appendix assumes a fixed set of orbitals  $\phi_i$  and a restricted formalism  $\phi_{i\uparrow} = \phi_{i\downarrow}$ . In this sense, the discussion considers the nature of restricted orbital functionals, rather than density functionals. Some form of (approximate) self-consistency cycles is required to determine the values of the orbitals, as described in Appendix C 2.

All systems we consider here have a nondegenerate ground state. Using

$$E_{x,S_k}^{\text{FDT}} := \frac{\partial \mathcal{E}_x^{\text{FDT}}}{\partial w_{S_k}} = -\frac{1}{2} \sum_{ij} \theta_{\max(i,j)}^{S_k} (ij|ji), \quad (\text{B1})$$

which was introduced as Eq. (9) in the main text, yields

$$E_{x,S_0}^{\text{FDT}} = - \sum_{i,j \in \{c,h\}} (ij|ji) = E_{x,S_0}^{\text{HF}} = \langle [c^2]h^2 | \hat{W} | [c^2]h^2 \rangle \quad (\text{B2})$$

$[[c]^2 \equiv 1^2 \dots (h-1)^2]$ , which follows trivially from the fact that  $\theta_{\max(i,j)}^{S_0} = 2 = \frac{1}{2} \theta_i^{S_0} \theta_j^{S_0}$  for all  $i$  and  $j$  being occupied and is zero otherwise. We remind the reader that

$$E_{x,\Phi}^{\text{HF}} = -\frac{1}{4} \sum_{\sigma} \sum_{ij} \theta_{i\sigma}^{\Phi} \theta_{j\sigma}^{\Phi} (ij|ji), \quad (\text{B3})$$

where  $\Phi$  indicates a Slater determinant and  $\theta_{i\sigma}^{\Phi} \in \{0, 1\}$  indicates the occupation factor of orbital  $i$  with spin  $\sigma$  in Slater-determinant state  $|\Phi\rangle$ . Using  $|\Phi_{S_0}\rangle = |[c^2]h^2\rangle$ ,  $|\Phi_{T_0}\rangle = |[c^2]h^{\uparrow}l^{\uparrow}\rangle$ , and  $|\Phi_{S_2}\rangle = |[c]^2l^2\rangle$  yields nonzero occupation factors:  $\theta_{i\uparrow}^{S_0} = \theta_{i\downarrow}^{S_0} = 1 \forall i \leq h$ ,  $\theta_{i\uparrow}^{T_0} = 1 \forall i \leq l$  and  $\theta_{i\downarrow}^{T_0} = 1 \forall i < h$ , and  $\theta_{i\uparrow}^{S_2} = \theta_{i\downarrow}^{S_2} = 1 \forall i < h, i = l$ .

We next consider the “H” energy expression,

$$\begin{aligned} \mathcal{E}_H^{\text{FDT}} &= \sum_{kk'} \min(w_{S_k}, w_{S_{k'}}) E_H[n_s^{S_k S_{k'}}] \\ &= \sum_{kk'} w_{S_{\max(k,k')}} E_H[n_s^{S_k S_{k'}}] \\ &= \sum_k w_{S_k} \left\{ E_H[n_s^{S_k S_k}] + 2 \sum_{k' < k} E_H[n_s^{S_k S_{k'}}] \right\}, \end{aligned}$$

where (see main text and Ref. [25])

$$E_H[n_s^{S_k S_{k'}}] := \int \frac{d\mathbf{r}d\mathbf{r}'}{2|\mathbf{r}-\mathbf{r}'|} n_s^{S_k S_{k'}}(\mathbf{r}) n_s^{S_k S_{k'}}(\mathbf{r}'), \quad (\text{B4})$$

$$n_s^{S_k S_{k'}} := \langle S_{s,k} | \hat{n} | S_{s,k'} \rangle, \quad (\text{B5})$$

and the latter expressions use the ensemble condition  $w_{S_k} \leq w_{S_{k'}}$  for  $k > k'$ . Then,

$$E_{H,S_k}^{\text{FDT}} = \frac{\mathcal{E}_H^{\text{FDT}}}{\partial w_{S_k}} = E_{H,S_k}^{\text{HF}} + 2 \sum_{k' < k} E_H[n_s^{S_k S_{k'}}], \quad (\text{B6})$$

where we introduced the shorthand

$$E_{H,S_k}^{\text{HF}} := E_H[n_s^{S_k S_k}] = \frac{1}{2} \sum_{ij} \theta_i^{S_k} \theta_j^{S_k} (ij|ij). \quad (\text{B7})$$

It follows trivially from  $S_0$  being the lowest-energy state that  $E_{H,S_0}^{\text{FDT}} = E_{H,S_0}^{\text{HF}}$ .

For completeness, we also note that

$$E_{\text{Hx},S_k} = \frac{\mathcal{E}_{\text{Hx}}}{\partial w_{S_k}} = \frac{\partial}{\partial w_{S_k}} \sum_k w_{S_k} \langle S_{s,k} | \hat{W} | S_{s,k'} \rangle = \langle S_{s,k} | \hat{W} | S_{s,k'} \rangle. \quad (\text{B8})$$

In the following we discuss the excited-state “x” energies for nondegenerate and some degenerate excited states. We shall also discuss “H” and “Hx” for the nondegenerate case.

### 1. Nondegenerate LUMO

Consider a nondegenerate single excitation, for which  $\theta_{i \in \{c\}}^{S_1} = 2$  and  $\theta_h^{S_1} = \theta_l^{S_1} = 1$  (all unspecified occupation factors here and henceforth are zero). We then obtain  $\theta_{\max(i,j)}^{S_1} = 2$  if  $i, j \in \{c\}$  or  $\theta_{\max(i,j)}^{S_1} = 1$  for all other combinations of occupied orbitals. By splitting the sum over core-core interactions we obtain

$$E_{x,S_1}^{\text{FDT}} = -\frac{1}{2} \sum_{i,j \in \{c\}} (ij|ji) - \frac{1}{2} \sum_{i,j \in \{c,h,l\}} (ij|ji) = E_{x,T_0}^{\text{HF}}, \quad (\text{B9})$$

where the expression  $E_{x,T_0}^{\text{HF}} = \langle [c^2]h^\uparrow l^\uparrow | \hat{W} | [c^2]h^\uparrow l^\uparrow \rangle = \langle [c^2]h^\downarrow l^\downarrow | \hat{W} | [c^2]h^\downarrow l^\downarrow \rangle$  is the same one that would be obtained for a triplet with core orbitals  $c$  with  $\downarrow$  spin and core, HOMO, and LUMO with  $\uparrow$  spin, i.e.,  $\theta_{i \in \{c,h,l\}}^{T_0} = 1$  and  $\theta_{i \in \{c\}}^{T_0} = 1$ .

The double excitation involves  $\theta_c = 2$ ,  $\theta_h = 0$ , and  $\theta_l = 2$ . We may then write

$$E_{x,S_2}^{\text{FDT}} = -\frac{1}{2} \sum_{i,j} \theta_{\max(i,j)}^{S_2} (ij|ji) = -\sum_{i,j \in \{c\}} (ij|ji) - 2 \sum_{i \in \{c\}} (il|li) - [2(hl|lh) + (ll|ll)] \quad (\text{B10})$$

using  $\theta_{\max(h,l)}^{S_2} = \theta_l^{S_2} = 2$ . It then follows that

$$\begin{aligned} 2E_{x,T_0}^{\text{HF}} - E_{x,S_0}^{\text{HF}} &= -\sum_{i,j \in \{c\}} (ij|ji) - \sum_{i,j \in \{c,h,l\}} (ij|ji) \\ &\quad + \sum_{i,j \in \{c,h\}} (ij|ji) \\ &= -\sum_{i,j \in \{c\}} (ij|ji) - 2 \sum_{i \in \{c\}, j \in \{h,l\}} (ij|ji) \\ &\quad - [(hh|hh) + 2(hl|lh) + (ll|ll)] \\ &\quad + 2 \sum_{i \in \{c\}} (ih|hi) + (hh|hh) \\ &= -\sum_{i,j \in \{c\}} (ij|ji) - 2 \sum_{i \in \{c\}} (il|li) - [2(hl|lh) \\ &\quad + (ll|ll)] \equiv E_{x,S_2}^{\text{FDT}}. \end{aligned} \quad (\text{B11})$$

Note, however, that

$$E_{x,S_2}^{\text{HF}} = -\sum_{ij \in \{c,l\}} (ij|ji) = E_{x,S_2}^{\text{FDT}} - 2(hl|lh) \neq E_{x,S_2}^{\text{FDT}}. \quad (\text{B12})$$

This is a surprising result since  $|S_{s,2}\rangle$  is a single Slater determinant and we might therefore expect it to have a Hartree-Fock “x” energy, whereas we instead find  $E_{x,S_2}^{\text{FDT}} \neq E_{x,S_2}^{\text{HF}}$ .

The above result for the double excitation also follows directly from Eq. (2) of the main text without algebra. Showing this involves first recognizing that  $f_h = 2w_{S_0} + w_{S_1}$  and  $f_l = w_{S_1} + 2w_{S_2}$  in general and that exchange depends on only occupation factors. We next recognize that the same  $f_h$  and  $f_l$  are attained from ensembles with  $\mathbf{w} = (w_{S_0}, w_{S_1}, w_{S_2})$  and  $\mathbf{w}' = (w_{S_0} - w_{S_2}, w_{S_1} + 2w_{S_2}, 0)$ . Therefore, both must yield the same exchange-energy expression,  $\mathcal{E}_x^{\text{FDT}} = (w_{S_0} - w_{S_2})E_{x,S_0}^{\text{HF}} + (w_{S_1} + 2w_{S_2})E_{x,T_0}^{\text{HF}}$ . Finally, taking the derivative with respect to  $w_{S_2}$  yields  $E_{x,S_2}^{\text{FDT}} = 2E_{x,T_0}^{\text{HF}} - E_{x,S_0}^{\text{HF}}$ . We recall that we are concerned with the form of orbital functionals here and treat orbitals as fixed—self-consistency would lead to different orbital inputs and different energies for different choices of ensemble weights.

To evaluate “H,” we require  $n_s^{S_k S_{k'}}$  for  $k' < k$  for use in Eq. (B6). They are

$$n_s^{S_1 S_0} = \sqrt{2} \phi_h \phi_l = n_s^{S_2 S_1}, \quad n_s^{S_2 S_0} = 0, \quad (\text{B13})$$

which we found by applying the Slater-Condon rules to  $|S_{s,0}\rangle = |[c^2]h^2\rangle$ ,  $|S_{s,1}\rangle = \frac{1}{\sqrt{2}}([c^2]h^\uparrow l^\downarrow - [c^2]h^\downarrow l^\uparrow)$  and  $|S_{s,2}\rangle = |[c^2]l^2\rangle$ . Therefore,

$$2E_{\text{H}}[n_s^{S_1 S_0}] = 2E_{\text{H}}[n_s^{S_2 S_1}] = 2(hl|lh), \quad (\text{B14})$$

which we recognize as the singlet-triplet splitting energy,  $E_{\text{ST}} := E_{\text{Hx},S_1} - E_{\text{Hx},T_0} = 2(hl|lh)$ . It follows from Eq. (B6) that

$$E_{\text{H},S_1}^{\text{FDT}} = E_{\text{H},S_1}^{\text{HF}} + E_{\text{ST}} = E_{\text{H},T_0}^{\text{HF}} + E_{\text{ST}}, \quad (\text{B15})$$

$$E_{\text{H},S_2}^{\text{FDT}} = E_{\text{H},S_2}^{\text{HF}} + E_{\text{ST}}, \quad (\text{B16})$$

where we used  $E_{\text{H},S_1}^{\text{HF}} = E_{\text{H},T_0}^{\text{HF}}$  since both KS states have the same density. Importantly, the FDT assigns  $E_{\text{ST}}$  to “H” rather than “x” for both single and double excitations.

Let us now briefly address “Hx.” By definition,  $E_{\text{Hx},S_1} = \langle S_{s,1} | \hat{W} | S_{s,1} \rangle = E_{\text{Hx},T_0} + E_{\text{ST}} = E_{\text{H},T_0}^{\text{HF}} + E_{x,T_0}^{\text{HF}} + E_{\text{ST}}$ . Since  $|S_{s,2}\rangle$  is already a single Slater determinant, we also obtain  $E_{\text{Hx},S_2} = \langle S_{s,2} | \hat{W} | S_{s,2} \rangle = E_{\text{H},S_2}^{\text{HF}} + E_{x,S_2}^{\text{HF}}$ . Scrutiny of Eq. (B11) reveals that  $E_{x,S_2}^{\text{FDT}}$  is the same as  $E_{x,S_2}^{\text{HF}}$ , except for the  $-2(hl|lh) = -E_{\text{ST}}$  term, and thus,  $E_{x,S_2}^{\text{HF}} = 2E_{x,T_0}^{\text{HF}} - E_{x,S_0}^{\text{HF}} + E_{\text{ST}}$ . Therefore,

$$\begin{aligned} E_{\text{Hx},S_1} &= E_{\text{H},T_0}^{\text{HF}} + E_{x,T_0}^{\text{HF}} + E_{\text{ST}} = [E_{\text{H},T_0}^{\text{HF}} + E_{\text{ST}}] + E_{x,T_0}^{\text{HF}} \\ &= E_{\text{H},S_1}^{\text{FDT}} + E_{x,S_1}^{\text{FDT}}, \end{aligned} \quad (\text{B17})$$

$$\begin{aligned} E_{\text{Hx},S_2} &= E_{\text{H},S_2}^{\text{HF}} + E_{x,S_2}^{\text{HF}} = E_{\text{H},S_2}^{\text{HF}} + [2E_{x,T_0}^{\text{HF}} - E_{x,S_0}^{\text{HF}} + E_{\text{ST}}] \\ &= [E_{\text{H},S_2}^{\text{HF}} + E_{\text{ST}}] + [2E_{x,T_0}^{\text{HF}} - E_{x,S_0}^{\text{HF}}] \\ &= E_{\text{H},S_2}^{\text{FDT}} + E_{x,S_2}^{\text{FDT}}, \end{aligned} \quad (\text{B18})$$

and we see that the sums are indeed correct.

Finally, we use the above results to write the “Hx” part of a hybrid. First, we recognize that a general pure-state DFA or hybrid DFA may be written as  $E_{\text{Hx}}^{\text{DFA}} = E_{\text{Hx}} + \bar{\alpha}[E_{x,S_2}^{\text{DFA}} - E_{x,S_2}^{\text{HF}}]$ , where  $\bar{\alpha} = 1 - \alpha$  is the complement to the Fock mixing



fraction  $\alpha$ . We next assume that

$$\mathcal{E}_{\text{Hx}}^{\text{DFA}} = \mathcal{E}_{\text{Hx}} + \bar{\alpha}[\mathcal{E}_{\text{x}}^{\text{DFA}} - \mathcal{E}_{\text{x}}^{\text{FDT}}] \quad (\text{B19})$$

is the appropriate ‘‘ensemblization.’’ With a KS ensemble,  $\hat{\Gamma}_s = \sum_{k=0}^2 w_{S_k} |S_{s,k}\rangle \langle S_{s,k}|$ , we use the results derived in this Appendix to obtain

$$\begin{aligned} \mathcal{E}_{\text{x}}^{\text{FDT}} &= w_{S_0} E_{\text{x},S_0}^{\text{FDT}} + w_{S_1} E_{\text{x},S_1}^{\text{FDT}} + w_{S_2} E_{\text{x},S_2}^{\text{FDT}} \\ &= w_{S_0} E_{\text{x},S_0}^{\text{HF}} + w_{S_1} E_{\text{x},T_0}^{\text{HF}} + w_{S_2} [2E_{\text{x},T_0}^{\text{HF}} - E_{\text{x},S_0}^{\text{HF}}] \\ &= (w_{S_0} - w_{S_2}) E_{\text{x},S_0}^{\text{HF}} + (w_{S_1} + 2w_{S_2}) E_{\text{x},T_0}^{\text{HF}}. \end{aligned} \quad (\text{B20})$$

Since our goal is to reuse standard DFA wherever possible, we next define

$$\mathcal{E}_{\text{x}}^{\text{DFA}} = (w_{S_0} - w_{S_2}) E_{\text{x},S_0}^{\text{DFA}} + (w_{S_1} + 2w_{S_2}) E_{\text{x},T_0}^{\text{DFA}} \quad (\text{B21})$$

in the same way. Finally, we obtain

$$\begin{aligned} \mathcal{E}_{\text{Hx}}^{\text{DFA}} &= \mathcal{E}_{\text{Hx}} + \bar{\alpha}[(w_{S_0} - w_{S_2})(E_{\text{x},S_0}^{\text{DFA}} - E_{\text{x},S_0}^{\text{HF}}) \\ &\quad + (w_{S_1} + 2w_{S_2})(E_{\text{x},T_0}^{\text{DFA}} - E_{\text{x},T_0}^{\text{HF}})], \end{aligned} \quad (\text{B22})$$

which is the equation in the main text and is defined using ensemble  $\mathcal{E}_{\text{Hx}}$  and well-known quantities and their approximations from pure-state DFT. We may also generalize to range-separated hybrid DFAs (rsDFAs; e.g.,  $\omega\text{B97X}$  [36]) by writing

$$\mathcal{E}_{\text{Hx}}^{\text{rsDFA}} := \mathcal{E}_{\text{Hx}} + \bar{\alpha}[\mathcal{E}_{\text{x}}^{\text{DFA}} - \mathcal{E}_{\text{x}}^{\text{FDT}}] + \beta[\mathcal{E}_{\text{x}}^{\text{DFA}(\omega)} - \mathcal{E}_{\text{x}}^{\text{FDT}(\omega)}] \quad (\text{B23})$$

$$\begin{aligned} &= \mathcal{E}_{\text{Hx}} + (w_{S_0} - w_{S_2})[\bar{\alpha}(E_{\text{x},S_0}^{\text{DFA}} - E_{\text{x},S_0}^{\text{HF}}) + \beta(E_{\text{x},S_0}^{\text{DFA}(\omega)} \\ &\quad - E_{\text{x},S_0}^{\text{HF}(\omega)})] + (w_{S_1} + 2w_{S_2})[\bar{\alpha}(E_{\text{x},T_0}^{\text{DFA}} - E_{\text{x},T_0}^{\text{HF}}) \\ &\quad + \beta(E_{\text{x},T_0}^{\text{DFA}(\omega)} - E_{\text{x},T_0}^{\text{HF}(\omega)})], \end{aligned} \quad (\text{B24})$$

where  $(\omega)$  denotes a short-range interaction with parameter  $\omega$  and  $\beta$  is the weight on short-range interactions. Note that  $E_{\text{H},S_k}^{\text{FDT}}$  are never required to determine  $\mathcal{E}_{\text{Hx}}^{\text{DFA}}$ , so we do not discuss them in the following degenerate cases.

## 2. Two- and threefold-degenerate LUMOs

The above expressions are not appropriate for single or double excitations into a degenerate LUMO. For this, we need to consider all possible single or double excitations and then average over the set. This yields the energy expressions

$$E_{\text{Hx},S_k} := \frac{1}{2} \sum_{ij} [F_{ij}^{J,S_k}(ij|ij) + F_{ij}^{K,S_k}(ij|ji)], \quad (\text{B25})$$

$$E_{\text{x},S_k}^{\text{FDT}} := -\frac{1}{2} \sum_{ij} f_{\max(i,j)}^{S_k}(ij|ji), \quad (\text{B26})$$

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  $F_{hl}^{J/K,S_k}$  and  $f_{h/l}^{S_k}$  are reported in Table I for LUMOs with up to threefold-degenerate LUMOs, i.e., for  $D_l \leq 3$ , where  $D_l$  is the LUMO degeneracy factor.

The first row of Table I may be obtained by recognizing that the ground state is completely independent of the LUMO, so its degeneracy can have no effect on the energy expressions. Therefore,  $F_{hl}^J = F_{hl}^K = F_{ll}^J = F_{ll}^K = 0$  is independent of  $D_l$ .

The second row is a little more difficult to obtain but can be derived without resorting to equations by recognizing that (i) each combination  $hl_q$  has the same energy, (ii) each combination  $hl_q$  is weighted by  $\frac{1}{D_l}$ , and (iii) all coefficients involving a LUMO are therefore linear in  $f_l = \frac{1}{D_l}$ . Since this result must also hold for  $D_l = 1$  and  $f_l = 1$ , we get the listed coefficients. The nondegenerate double excitation described in the third row may be represented by a single Slater determinant with  $\theta_c = \theta_l = 2$  and  $\theta_h = 0$ , so it takes its expected form. Next we derive the final two rows for two- and threefold-degenerate LUMOs.

A twofold-degenerate LUMO, induced by cylindrical symmetry, can yield three singlet states:  $|S_{l^2,D}\rangle \in \{|l_1 l_2\rangle, |l_1 l_1\rangle, |l_2 l_2\rangle\}$ , where the notation refers to which of the two ( $l_1$  or  $l_2$ ) degenerate orbitals is occupied in the singlet state. All states give the same kinetic energy, external energy, and core-LUMO energy.

We may thus obtain the ensemble ‘‘Hx’’ energy [23] by finding the lowest eigenvalues of

$$[\mathbb{W}]_{DD'} = \langle S_{l^2,D} | \hat{W} | S_{l^2,D'} \rangle. \quad (\text{B27})$$

Ignoring core contributions, which are the same in all cases, yields

$$\mathbb{W} = \begin{pmatrix} (l_1 l_2 | l_1 l_2) + (l_1 l_2 | l_2 l_1) & 0 & 0 \\ 0 & (l_1 l_1 | l_1 l_1) & (l_1 l_2 | l_2 l_1) \\ 0 & (l_1 l_2 | l_2 l_1) & (l_2 l_2 | l_2 l_2) \end{pmatrix} \quad (\text{B28})$$

after using the Slater-Condon rules. Then, we can use  $(l_1 l_1 | l_1 l_1) = (l_2 l_2 | l_2 l_2) = (l_1 l_2 | l_1 l_2) + 2(l_1 l_2 | l_2 l_1)$  (from symmetry) to show that the lowest eigenvalue  $W_1 = W_2 = (l_1 l_2 | l_1 l_2) + (l_1 l_2 | l_2 l_1)$  of  $\mathbb{W}$  is twofold degenerate, while the third is  $W_3 = (l_1 l_2 | l_1 l_2) + 3(l_1 l_2 | l_2 l_1)$ . In terms of CSFs, we thus obtain twofold-degenerate double-excitation states:

$$|S_{2,1}\rangle = \frac{1}{\sqrt{2}} (|[c^2]l_1^\uparrow l_2^\downarrow\rangle - |[c^2]l_1^\downarrow l_2^\uparrow\rangle), \quad (\text{B29})$$

$$|S_{2,2}\rangle = \frac{1}{\sqrt{2}} (|[c^2]l_1^\uparrow l_1^\downarrow\rangle - |[c^2]l_2^\downarrow l_2^\uparrow\rangle). \quad (\text{B30})$$

Both  $l_1$  and  $l_2$  are equally occupied in these states, giving  $f_{l_1} = f_{l_2} \equiv f_l = 1$ .

The ‘‘Hx’’ energy is equal to the lowest eigenvalue, i.e.,

$$E_{\text{Hx},S_2} = W_1 = W_2 = (l_1 l_2 | l_1 l_2) + (l_1 l_2 | l_2 l_1), \quad (\text{B31})$$

which is also equal to  $E_{\text{Hx},S_2} = \frac{1}{2} \sum_{pq} [F_{l_p l_q}^J(pq|pq) + F_{l_p l_q}^K(pq|qp)]$ . However, because of the symmetry, neither  $F^J$  nor  $F^K$  can depend on our choice of  $l_p$  and  $l_q$ . Thus, we seek to find  $F^J$  and  $F^K$  in

$$\begin{aligned} E_{\text{Hx},S_2} &= (l_1 l_2 | l_1 l_2) + (l_1 l_2 | l_2 l_1) \\ &= \frac{1}{2} \sum_{pq \in \{1,2\}} [F^J(l_p l_q | l_p l_q) + F^K(l_p l_q | l_q l_p)] \\ &= F^J[(l_1 l_1 | l_1 l_1) + (l_1 l_2 | l_2 l_1)] \\ &\quad + F^K[(l_1 l_1 | l_1 l_1) + (l_1 l_2 | l_2 l_1)] \\ &= F^J[2(l_1 l_2 | l_1 l_2) + 2(l_1 l_2 | l_2 l_1)] \end{aligned}$$

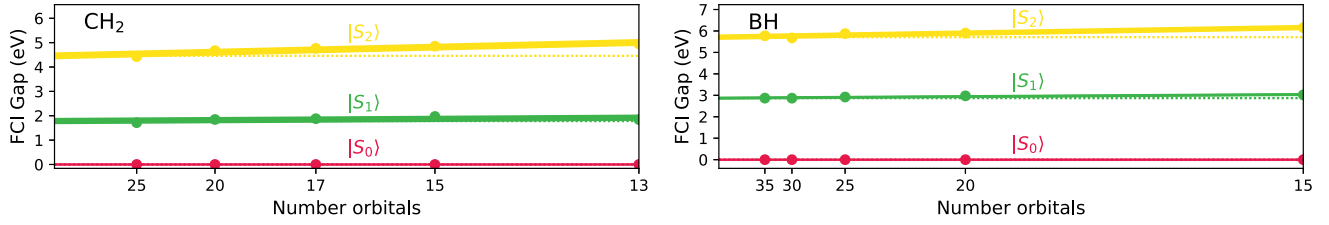


FIG. 5. FCI energies (eV) for CH<sub>2</sub> (left) and BH (right) shown as a function of the inverse cube of the size of the active space (values are shown on the  $x$  ticks). Solid lines are a linear fit to the data, and dashed lines indicate the value extrapolated to the complete-basis-set ( $N_a \rightarrow \infty$ ) limit.

$$\begin{aligned}
 & + F^K [(l_1 l_2 | l_1 l_2) + 3(l_1 l_2 | l_2 l_1)] \\
 & = (2F^J + F^K)(l_1 l_2 | l_1 l_2) + (2F^J + 3F^K)(l_1 l_2 | l_2 l_1),
 \end{aligned} \tag{B32}$$

where we again used  $(l_1 l_1 | l_1 l_1) = (l_1 l_2 | l_1 l_2) + 2(l_1 l_2 | l_2 l_1)$  and invariance to permutations of  $l_1$  and  $l_2$ . Solving for  $F^J$  and  $F^K$  in  $2F^J + F^K = 1$  and  $2F^J + 3F^K = 1$  finally yields  $F^J = \frac{1}{2}$  and  $F^K = 0$ .

Similar reasoning applied to a threefold-degenerate LUMO gives

$$|S_{2,1}\rangle = \frac{1}{\sqrt{2}} (|[c^2]l_1^\uparrow l_2^\downarrow\rangle - |[c^2]l_1^\downarrow l_2^\uparrow\rangle), \tag{B33}$$

$$|S_{2,2}\rangle = \frac{1}{\sqrt{2}} (|[c^2]l_1^\uparrow l_3^\downarrow\rangle - |[c^2]l_1^\downarrow l_3^\uparrow\rangle), \tag{B34}$$

$$|S_{2,3}\rangle = \frac{1}{\sqrt{2}} (|[c^2]l_2^\uparrow l_3^\downarrow\rangle - |[c^2]l_2^\downarrow l_3^\uparrow\rangle), \tag{B35}$$

and

$$|S_{2,4}\rangle = \frac{1}{\sqrt{2}} (|[c^2]l_1^\uparrow l_1^\downarrow\rangle - |[c^2]l_2^\downarrow l_2^\uparrow\rangle), \tag{B36}$$

$$|S_{2,5}\rangle = \frac{1}{\sqrt{6}} (2|[c^2]l_3^\uparrow l_3^\downarrow\rangle - |[c^2]l_1^\uparrow l_1^\downarrow\rangle - |[c^2]l_2^\downarrow l_2^\uparrow\rangle) \tag{B37}$$

for the fivefold-degenerate double excitation (equivalent to the  $d$  orbitals), all with  $W_K = (l_1 l_2 | l_1 l_2) + (l_1 l_2 | l_2 l_1)$ . Taking an average over these five states gives  $l_1$ ,  $l_2$ , and  $l_3$  all equally occupied (as also required by symmetry). Thus,  $f_{l_1} = f_{l_2} = f_{l_3} \equiv f_l = \frac{2}{3}$ .

The “Hx” energy is again

$$E_{\text{Hx}} = W_{1\dots 5} = (l_1 l_2 | l_1 l_2) + (l_1 l_2 | l_2 l_1). \tag{B38}$$

Following the same steps as the twofold-degenerate case considered above yields

$$\begin{aligned}
 E_{\text{Hx}, S_2} & = \frac{1}{2} \sum_{pq \in \{1,2,3\}} [F^J (l_p l_q | l_p l_q) + F^K (l_p l_q | l_q l_p)] = \frac{1}{2} F^J [3(l_1 l_1 | l_1 l_1) + 6(l_1 l_2 | l_1 l_2)] + \frac{1}{2} F^K [3(l_1 l_1 | l_1 l_1) + 6(l_1 l_2 | l_2 l_1)] \\
 & = F^J [9(l_1 l_2 | l_1 l_2) + 6(l_1 l_2 | l_2 l_1)] + F^K [3(l_1 l_2 | l_1 l_2) + 12(l_1 l_2 | l_2 l_1)] \\
 & = (9F^J + 3F^K)(l_1 l_2 | l_1 l_2) + (6F^J + 12F^K)(l_1 l_2 | l_2 l_1).
 \end{aligned} \tag{B39}$$

Finally, solving the simultaneous equations lets us obtain  $F^J = \frac{1}{5}$  and  $F^K = \frac{1}{15}$ .

## APPENDIX C: DETAILS OF EDFT CALCULATIONS AND BENCHMARKS

### 1. Benchmarks for CH<sub>2</sub> and BH

Highly accurate benchmark energies for Be and nitroxyl, among other benchmarks, were recently reported in Ref. [1]. However, most of the systems studied in that work have strongly correlated ground and/or excited states, which complicates our present goal of deriving EDFA for doubly excited states, not strongly correlated states.

We thus supplement Be and nitroxyl by benchmark reference values for BH and CH<sub>2</sub>, both of which are weakly correlated. To obtain our benchmark values we carry out fully variational full-configuration-interaction (FCI) calculations in PSI4 [56,57] on the molecules using correlation-consistent

basis sets [58]. Final values are obtained using CC-PVTZ for CH<sub>2</sub> (note that CC-PVQZ gave consistently higher energies for the incomplete active spaces considered here) and CC-PVQZ for BH, with varying numbers  $N_a$  of orbitals in the active space— $1s$  orbitals are always kept frozen to reduce costs. We then extrapolate to the complete-active-space limit by fitting  $E_{S_2} - E_{S_0}$  as a function of  $1/N_a^3$  for different values of  $N_a$ . Figure 5 shows gaps as a function of the inverse cube of the active space size  $N_a$ , which illustrates that this is a reasonable fit. We thus obtain double-excitation gaps of 4.50 eV for CH<sub>2</sub> and 5.70 eV for BH. We can also use the results to estimate a reasonable error bar to be around  $\pm 0.15$  eV, which is more than sufficient for our purposes.

### 2. EDFT calculations

We begin this section by describing mathematically the problem we solve and then move on to technical details. In

TABLE II. Nitroxyl gaps predicted by a computationally feasible optimization (involving all orbitals within 10 eV of the HOMO) and using SEGKS [32]. SEGKS provides consistently lower energies and is thus used in the main text.

DFA	PBE	PBE0	xPBE <sub>0.00</sub>	xPBE <sub>0.20</sub>	xPBE <sub>0.40</sub>	xPBE <sub>0.60</sub>	xPBE <sub>0.80</sub>	xPBE <sub>1.00</sub>
Optimization	5.21	5.15	4.99	4.93	5.00	5.07	5.21	5.40
SEGKS	4.98	4.95	4.74	4.72	4.77	4.85	4.92	5.01

our self-consistent EDFT calculations we evaluate

$$\mathcal{E} = \mathcal{T}_s + \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + \mathcal{E}_{\text{Hxc}}^{\text{DFA}} \quad (\text{C1})$$

using an ensembled hybrid approximation (see the main text for general details):

$$\begin{aligned} \mathcal{E}_{\text{Hxc}}^{\text{DFA}} := & \mathcal{E}_{\text{Hxc}} + (1 - 2w)\{\bar{\alpha}(E_{x,S_0}^{\text{DFA}} - E_{x,S_0}^{\text{FDT}}) + E_{c,S_0}^{\text{DFA}}\} \\ & + 2w\{\bar{\alpha}(E_{x,T_0}^{\text{DFA}} - E_{x,T_0}^{\text{FDT}}) + E_{c,T_0}^{\text{DFA}}\} \end{aligned} \quad (\text{C2})$$

for  $0 \leq w \leq \frac{1}{2}$ , which is equivalent to setting  $w_{S_0} = 1 - w$ ,  $w_{S_1} = 0$ , and  $w_{S_2} = w$ , where  $w$  is the fraction of double excitation. It is important to note that this choice of weight *prima facie* breaches the Gross-Oliveira-Kohn theorems [11,12], which require decreasing weights for increasing excitation levels. However, in the case of BH and Be it can be rigorously justified because the ground, single excited, and double excited states all belong to different symmetry groups and are thus subject to more general theorems [28]. This argument does not apply to CH<sub>2</sub> and nitroxyl. But in practice we observe no apparent problems for self-consistency.

Setting  $w_{S_1} = 0$  has the practical benefit that the ensemble is described only by a single weight  $w$ . More importantly, it lets us overcome errors caused by the neglect of the density-driven (DD) correlation energy [24] that accounts for the difference between ensemble KS densities and the true densities of the interacting systems. (Note the DD correlation errors appear in both exact and approximate theories, which makes them different from density-driven errors caused by approximations to the effective KS potential.) These density differences mean that the true (up to DFA errors) ensemble energy at weight  $w$  is  $\mathcal{E}^{\text{SD},w} + \mathcal{E}_c^{\text{DD},w}$ , where  $\mathcal{E}^{\text{SD},w}$  is given by Eq. (C1) and where, by definition,  $\mathcal{E}_c^{\text{DD},w=0} = \mathcal{E}_c^{\text{DD},w=1} = 0$  for both pure-state limits but is otherwise nonzero. Despite DD correlations not contributing at  $w = 1$  [59], a problem arises because we cannot self-consistently evaluate (C1) for  $w = 1$  due to variational collapse to the ground state. A more detailed practical description of the problem (and its solution, below) is described in the Supplementary Material of Ref. [32].

Fortunately, the single-parameter model offers a simple fix, via the procedure discussed in Ref. [32], to extrapolate EDFT results from  $0 \leq w \leq \frac{1}{2}$  (which may be solved self-consistently) out to pure-state  $w = 1$  (which cannot be solved self-consistently). We are thereby able to obtain energies that are approximately free from density-driven correlation errors. Algorithmically, this involves (i) computing  $\mathcal{E}(w)$  [Eq. (C1)] for  $w \in \{0, \frac{1}{8}, \frac{1}{4}, \frac{3}{8}, \frac{1}{2}\}$ , (ii) fitting a quadratic  $\mathcal{E}^{\text{quad}}(w)$  to  $\mathcal{E}(w)$ , and (iii) using the fit to evaluate

$$E_{S_0} = \mathcal{E}^{\text{quad}}(w = 0), \quad E_{S_2} = \mathcal{E}^{\text{quad}}(w = 1), \quad (\text{C3})$$

The values of  $E_{S_0}$  and  $E_{S_2}$  so obtained may thus be used for our predicted excitation energy:  $\Delta E_{S_2} = E_{S_2} - E_{S_0} = \mathcal{E}^{\text{quad}}(w = 1) - \mathcal{E}^{\text{quad}}(w = 0)$ .

EDFT calculations are carried out using a customized PYTHON3 code using routines from PSI4 [56,57] and employing an algorithmic approach similar to the code described in Ref. [29] to give benchmark values. We carry out EDFT calculations for Be using the DEF2-QZVPP [60] basis set, as the  $2p$  orbital benefits from the additional  $p$  bases. We use the DEF2-TZVP [60] basis set for CH<sub>2</sub>, BH, and nitroxyl, whose electrons are more tightly bound. All code is available on request.

For Be, CH<sub>2</sub>, and BH, initial ground-state orbitals are iteratively reoptimized over unitary transformations until the ensemble energy [Eq. (C1)] is minimized to within less than 0.01 eV. The code preserves symmetries by applying the same unitary transformation to all degenerate states. It provides a rigorous upper bound to the EDFT gap.

For nitroxyl, it becomes too costly to use this approach due to the large number of orbitals required to provide a good upper bound. Thus, we instead employ the simplified ensemble generalized Kohn-Sham (SEGKS) approach [29,32], which gives lower energies than a full optimization involving all orbitals within 10 eV of the HOMO and provides a better upper bound to the gap (see Table II).

### 3. CCSD and CC3 calculations

Finally, we note that our CCSD and CC3 excitation energies are obtained using EOM-CCSD [51] and EOM-CC3 [52]. They use the same basis sets as the ensemble DFT calculations and are computed using default routines in PSI4.

### APPENDIX D: DETAILS OF RPA CALCULATIONS

In density functional theory, the interacting density-density response function  $\chi_\lambda$  with an interaction strength  $\lambda$  is related to the noninteracting KS response function  $\chi_s$  (at  $\lambda = 0$ ) via [25,38]

$$\begin{aligned} \chi_\lambda(\mathbf{r}, \mathbf{r}') = & \chi_s(\mathbf{r}, \mathbf{r}') + \int d\mathbf{r}_2 d\mathbf{r}_3 \chi_s(\mathbf{r}, \mathbf{r}_2) \\ & \times [\lambda W(\mathbf{r}_2, \mathbf{r}_3) + f_{\text{xc},\lambda}(\mathbf{r}_2, \mathbf{r}_3)] \chi_\lambda(\mathbf{r}_3, \mathbf{r}'), \end{aligned} \quad (\text{D1})$$

or  $\hat{\chi}_\lambda = \hat{\chi}_s + \hat{\chi}_s[\lambda \hat{W} + \hat{f}_{\text{xc},\lambda}] \hat{\chi}_\lambda$  in a convenient operator notation. The correlation energy of any quantum system may then be evaluated from the response functions using the adiabatic connection formula with the fluctuation-dissipation theorem [25,38] (ACFD), giving

$$E_c = - \int_0^1 d\lambda \int_0^\infty \frac{d\omega}{2\pi} \text{Tr}[(\hat{\chi}_\lambda - \hat{\chi}_s) \hat{W}]. \quad (\text{D2})$$

The random-phase approximation (RPA) consists of setting  $f_{xc,\lambda} = 0$  in (D1) so that  $\hat{\chi}_\lambda^{\text{RPA}} = \hat{\chi}_s + \lambda \hat{\chi}_s \hat{W} \hat{\chi}_\lambda^{\text{RPA}}$ . Then,  $E_c^{\text{RPA}} = \int_0^\infty \frac{d\omega}{2\pi} \text{Tr}[\log_{10}(1 - \hat{\chi}_s \hat{W}) + \hat{\chi}_s \hat{W}]$  follows by analytically integrating over  $\lambda$  in Eq. (D2). The RPA has been used to successfully study chemical and solid-state interactions due to its ability to seamlessly capture different bonding types [39–42]. However, it does have limitations in describing systems with open-shell character [45–47] as the exclusion of  $f_x$  leads to spurious self-interaction errors.

One can readily adapt the RPA to ensembles by using the response function [Eq. (A9)] from Appendix A in

$$\mathcal{E}_c^{\text{RPA}} := \int_0^\infty \frac{d\omega}{2\pi} \text{Tr}[\ln(1 - \hat{\chi}_s \hat{W}) + \hat{\chi}_s \hat{W}], \quad (\text{D3})$$

which is the most direct translation of the RPA to ensembles. We denote this the ensemble RPA correlation-energy functional. A first step toward evaluating Eq. (D3) efficiently involves rewriting Eq. (A9) as

$$\chi_s(\mathbf{r}, \mathbf{r}'; i\omega) := \sum_{ia} Q_{ia}(i\omega) \phi_i(\mathbf{r}) \phi_a(\mathbf{r}) \phi_i(\mathbf{r}') \phi_a(\mathbf{r}'), \quad (\text{D4})$$

where  $ia$  indicates all pairs obeying  $f_i \neq f_a$  and  $\epsilon_i \neq \epsilon_a$ , for which  $Q_{ia} = \frac{(f_i - f_j)(\epsilon_i - \epsilon_j)}{(\epsilon_i - \epsilon_j)^2 + \omega^2}$  is nonzero. It is then straightforward to show that

$$\text{Tr}[\hat{\chi}_s \hat{W}] = \int \frac{d\mathbf{r}_1 d\mathbf{r}_2}{|\mathbf{r}_2 - \mathbf{r}_1|} \chi_s(\mathbf{r}_1, \mathbf{r}_2) = \sum_{ia} Q_{ia}(ia|ia), \quad (\text{D5})$$

$$\begin{aligned} \text{Tr}[\hat{\chi}_s \hat{W} \hat{\chi}_s \hat{W}] &= \int \frac{d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4}{|\mathbf{r}_3 - \mathbf{r}_2| |\mathbf{r}_1 - \mathbf{r}_4|} \chi_s(\mathbf{r}_1, \mathbf{r}_2) \chi_s(\mathbf{r}_3, \mathbf{r}_4) \\ &= \sum_{ia,jb} Q_{ia}(ia|jb) Q_{jb}(jb|ia), \end{aligned} \quad (\text{D6})$$

$$\text{Tr}[(\hat{\chi}_s \hat{W})^3] = \sum_{ia,jb,kc} Q_{ia}(ia|jb) Q_{jb}(jb|kc) Q_{kc}(kc|ia) \quad (\text{D7})$$

are equal to  $\text{Tr}[\mathbb{X}]$ ,  $\text{Tr}[\mathbb{X}^2]$ , and  $\text{Tr}[\mathbb{X}^3]$ , respectively, for  $[\mathbb{X}(i\omega)]_{ia,jb} = \sqrt{Q_{ia}(i\omega) Q_{jb}(i\omega)} (ia|jb)$ . It is straightforward to show, by induction, that the relationship continues for higher powers.

It follows that  $\mathcal{E}_c^{\text{RPA}} = \int \frac{d\omega}{2\pi} \text{Tr}[\ln[1 - \mathbb{X}(i\omega)] - \mathbb{X}(i\omega)]$ . Clenshaw-Curtis quadrature lets us obtain a set of abscissas  $\omega_i$  and weights  $\xi_i$  to accurately approximate the frequency integral  $\int f(i\omega) d\omega \approx \sum_i \xi_i f(i\omega_i)$ . We thus finally evaluate

$$\mathcal{E}_c^{\text{RPA}} = \sum_i \frac{\xi_i}{2\pi} \left\{ \sum_k \left[ \log_{10}[1 - x_k(i\omega_i)] + x_k(i\omega_i) \right] \right\} \quad (\text{D8})$$

using eigenvalues  $x_k(i\omega_i)$  of  $\mathbb{X}(i\omega_i)$ . The term in the large curly brackets depends rather smoothly on  $\omega$ . Equation (D8) may therefore be evaluated using a modest number of abscissas.

Two additional points need to be discussed. First, although  $Q_{ia}$  is analytic, it does depend on orbitals  $\phi_i$  and their energies  $\epsilon_i$ , which should account for the ensemble nature of the problem. For the orbitals, we use ensemble PBE results extrapolated to the double-state  $w \rightarrow 1$  limit. However, the ensemble equations do not obey a unique orbital equation [29]. Thus, for the energies, we use

$$\epsilon_i \approx \int d\mathbf{r} \phi_i(\mathbf{r}) \left[ -\frac{1}{2} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + \tilde{v}_{\text{Hxc}}^{\text{PBE}}(\mathbf{r}) \right] \phi_i(\mathbf{r}), \quad (\text{D9})$$

where  $\tilde{v}_{\text{Hxc}}^{\text{PBE}}$  is the PBE Hartree, exchange, and correlation potential evaluated at the ground-state density. For the illustrative purposes employed here this is a reasonable approximation.

Second, we need to evaluate  $(ia|jb)$  efficiently. For this, we use an orthonormalized  $[\int \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} P_\mu(\mathbf{r}) P_\nu(\mathbf{r}') = \delta_{\mu\nu}]$  density-fitting basis [61] (DEF2-TZVP-RI for CH<sub>2</sub>, BH, and nitroxyl and DEF2-QZVPP-RI for Be),  $P_\mu(\mathbf{r})$ , in which coefficients  $C_{ia,\mu}$  in  $\phi_i(\mathbf{r}) \phi_a(\mathbf{r}) = \sum_\mu C_{ia,\mu} P_\mu(\mathbf{r})$  are evaluated once, to obtain  $(ia|jb) = \sum_\mu C_{ia,\mu} C_{jb,\mu}$  in separable form. Thus, we may trivially evaluate

$$X_{iq,jb}(i\omega) = \sqrt{Q_{ia}(i\omega) Q_{jb}(i\omega)} \sum_\mu C_{ia,\mu} C_{jb,\mu} \quad (\text{D10})$$

for arbitrary  $\omega$ , without storing  $(ia|jb)$ . All code is available on request.

## APPENDIX E: DETAILS FOR CALCULATIONS USING EQ. (17)

As discussed in the main text, Eq. (11) can be evaluated using existing DFA implementations, and self-consistency can be approximated using the methods described in Appendix C. By contrast, calculations using Eq. (17) introduce two complications. First, they require explicit implementation of the DFA( $\tilde{\zeta}^{\text{ot}}$ ) correlation-energy part of Eq. (17); the examples and following discussion use PBE as the DFA. Second, they cannot be evaluated self-consistently.

Addressing the first point requires modification of the numerical integration scheme used to compute density functionals. We therefore compute the density  $n_r$ , on-top pair distribution  $P_{x,r}$ , and reduced gradient  $s_r$  on a grid labeled by  $\mathbf{r}$ . We then use standard routines from PSI4 to compute

$$E_c = \sum_{\mathbf{r}} w_r n_r \epsilon_x^{\text{PBE}}(n_r, s_r, \tilde{\zeta}_r^{\text{ot}}), \quad (\text{E1})$$

$$\tilde{\zeta}_r^{\text{ot}} = \min \left( \frac{\sqrt{-2P_{x,r} - n_r^2}}{n_r}, \frac{n_r}{\sqrt{-2P_{x,r} - n_r^2}} \right). \quad (\text{E2})$$

Abscissas  $\mathbf{r}$  and weights  $w_r$  are from the default quadrature scheme in PSI4.

To address the second point, PBE/PBE0( $\tilde{\zeta}^{\text{ot}}$ ) correlation energies are obtained by first computing xPBE<sub>0/0.25</sub> energies per Appendix C. Then, we compute correlation energies using (E2) evaluated using ensemble Hartree-Fock orbitals and density with an equal mixture of ground and double excitations. Applying similar assumptions to regular PBE correlation energies gives errors of <0.1 eV compared to fully self-consistent calculations, which is suitable for present purposes. All code is available on request.

## APPENDIX F: DOUBLE EXCITATIONS IN H<sub>2</sub>

We evaluate the PBE and PBE0 energies of the H<sub>2</sub> diatom using the same self-consistent procedure (for PBE and PBE0) as in the previous Appendixes, with DEF2-TZVP as the basis set, using Eq. (C2). Calculations are carried out for the singlet states involving only the first two  $\sigma$  orbitals:  $\phi_0 = \phi_{\sigma_g} \rightarrow [\phi_{1s,L} + \phi_{1s,R}]/\sqrt{2}$  and  $\phi_1 = \phi_{\sigma_u} \rightarrow$

$[\phi_{1s,L} - \phi_{1s,R}]/\sqrt{2}$ , where  $L$  and  $R$  represent left and right atoms and  $\rightarrow$  indicates the dissociation limit. We evaluate  $\text{PBE}(\tilde{\zeta}^{\text{ot}})$  and  $\text{PBE0}(\tilde{\zeta}^{\text{ot}})$  partially self-consistently by using self-consistent  $\text{xPBE}_{0.00/0.25}$  as a starting point and then adding correlation energies computed using Eq. (11) of the main text, evaluated with  $\text{xPBE}_{0.00}$  orbitals and densities.

The large  $D$  expansion of this excitation is interesting, as the correct gap obeys  $\frac{1}{2} - \frac{1}{D}$  Ha for  $D$  in atomic units. Approximations asymptote to  $\Delta E^{\text{DFA}}(D) \rightarrow \Delta E_{\infty} + \frac{Z_{\infty}}{D}$ . Thus,

in any DFA there are two constants of interest:  $\Delta E_{\infty}$  (should be 13.6 eV) and  $Z_{\infty}$  (should be 1). Asymptotically, we find that PBE gives  $\Delta E_{\infty} = 8.94$  eV and  $Z_{\infty} = 1$ , while we obtain 9.48 eV and 1 for  $\text{PBE}(\tilde{\zeta}^{\text{ot}})$ , meaning both have the correct coefficient for the inverse  $D$  term but not the correct asymptotic gap. PBE0 and  $\text{PBE0}(\tilde{\zeta}^{\text{ot}})$  yield  $\Delta E_{\infty} = 7.28$  and 6.61 eV, respectively, both with an incorrect  $Z_{\infty} = \frac{3}{4}$ . Ensemble Hartree-Fock is by far the worst case, yielding  $\Delta E_{\infty} = 0$  eV and  $Z_{\infty} = 0$ . All code is available on request.

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- [1] P.-F. Loos, M. Boggio-Pasqua, A. Scemama, M. Caffarel, and D. Jacquemin, Reference energies for double excitations, *J. Chem. Theory Comput.* **15**, 1939 (2019).
- [2] P. Hohenberg and W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* **136**, B864 (1964).
- [3] W. Kohn and L. J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* **140**, A1133 (1965).
- [4] S. Kümmel and L. Kronik, Orbital-dependent density functionals: Theory and applications, *Rev. Mod. Phys.* **80**, 3 (2008).
- [5] R. O. Jones, Density functional theory: Its origins, rise to prominence, and future, *Rev. Mod. Phys.* **87**, 897 (2015).
- [6] O. Gunnarsson and B. I. Lundqvist, Exchange and correlation in atoms, molecules, and solids by the spin-density-functional formalism, *Phys. Rev. B* **13**, 4274 (1976).
- [7] E. Runge and E. K. U. Gross, Density-Functional Theory for Time-Dependent Systems, *Phys. Rev. Lett.* **52**, 997 (1984).
- [8] N. T. Maitra, F. Zhang, R. J. Cave, and K. Burke, Double excitations within time-dependent density functional theory linear response, *J. Chem. Phys.* **120**, 5932 (2004).
- [9] P. Romaniello, D. Sangalli, J. A. Berger, F. Sottile, L. G. Molinari, L. Reining, and G. Onida, Double excitations in finite systems, *J. Chem. Phys.* **130**, 044108 (2009).
- [10] P. Elliott, S. Goldson, C. Canahui, and N. T. Maitra, Perspectives on double-excitations in TDDFT, *Chem. Phys.* **391**, 110 (2011).
- [11] E. K. U. Gross, L. N. Oliveira, and W. Kohn, Rayleigh-Ritz variational principle for ensembles of fractionally occupied states, *Phys. Rev. A* **37**, 2805 (1988).
- [12] E. K. U. Gross, L. N. Oliveira, and W. Kohn, Density-functional theory for ensembles of fractionally occupied states. I. Basic formalism, *Phys. Rev. A* **37**, 2809 (1988).
- [13] L. N. Oliveira, E. K. U. Gross, and W. Kohn, Density-functional theory for ensembles of fractionally occupied states. II. Application to the He atom, *Phys. Rev. A* **37**, 2821 (1988).
- [14] Z.-H. Yang, A. Pribram-Jones, K. Burke, and C. A. Ullrich, Direct Extraction of Excitation Energies from Ensemble Density-Functional Theory, *Phys. Rev. Lett.* **119**, 033003 (2017).
- [15] F. Sagredo and K. Burke, Accurate double excitations from ensemble density functional calculations, *J. Chem. Phys.* **149**, 134103 (2018).
- [16] P.-F. Loos and E. Fromager, A weight-dependent local correlation density-functional approximation for ensembles, *J. Chem. Phys.* **152**, 214101 (2020).
- [17] C. Marut, B. Senjean, E. Fromager, and P.-F. Loos, Weight dependence of local exchange-correlation functionals in ensemble density-functional theory: Double excitations in two-electron systems, *Faraday Discuss.* **224**, 402 (2020).
- [18] M. Filatov and S. Shaik, A spin-restricted ensemble-referenced Kohn-Sham method and its application to diradicaloid situations, *Chem. Phys. Lett.* **304**, 429 (1999).
- [19] M. Filatov, M. Huix-Rotllant, and I. Burghardt, Ensemble density functional theory method correctly describes bond dissociation, excited state electron transfer, and double excitations, *J. Chem. Phys.* **142**, 184104 (2015).
- [20] M. Filatov, Spin-restricted ensemble-referenced Kohn-Sham method: Basic principles and application to strongly correlated ground and excited states of molecules, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **5**, 146 (2015).
- [21] 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, Cham, 2016), pp. 97–124.
- [22] T. Gould and J. F. Dobson, The flexible nature of exchange, correlation, and Hartree physics: Resolving “delocalization” errors in a “correlation free” density functional, *J. Chem. Phys.* **138**, 014103 (2013).
- [23] T. Gould and S. Pittalis, Hartree and Exchange in Ensemble Density Functional Theory: Avoiding the Nonuniqueness Disaster, *Phys. Rev. Lett.* **119**, 243001 (2017).
- [24] T. Gould and S. Pittalis, Density-Driven Correlations in Many-Electron Ensembles: Theory and Application for Excited States, *Phys. Rev. Lett.* **123**, 016401 (2019).
- [25] T. Gould, G. Stefanucci, and S. Pittalis, Ensemble Density Functional Theory: Insight from the Fluctuation-Dissipation Theorem, *Phys. Rev. Lett.* **125**, 233001 (2020).
- [26] E. Fromager, Individual Correlations in Ensemble Density-Functional Theory: State-Driven/Density-Driven Decompositions without Additional Kohn-Sham Systems, *Phys. Rev. Lett.* **124**, 243001 (2020).
- [27] We further assume that no other singly excited state has an energy lower than that of  $|S_2\rangle$ .
- [28] T. Gould and S. Pittalis, Density-driven correlations in ensemble density functional theory: Insights from simple excitations in atoms, *Aust. J. Chem.* **73**, 714 (2020).
- [29] T. Gould and L. Kronik, Ensemble generalized Kohn-Sham theory: The good, the bad, and the ugly, *J. Chem. Phys.* **154**, 094125 (2021).
- [30] Specifically, minimization is over ensembles  $\hat{\Gamma}_w$  with weights  $w$ , yielding the target density  $\text{Tr}[\hat{\Gamma}_w \hat{n}] = n$ .
- [31] The fact that in EDFT KS states must be noninteracting CSFs can be understood via group theory and derived procedurally

- when evaluating  $\mathcal{E}_{\text{HX}}$  via (degenerate) perturbation theory; some examples are provided in Appendix B.
- [32] T. Gould, Approximately self-consistent ensemble density functional theory: Toward inclusion of all correlations, *J. Phys. Chem. Lett.* **11**, 9907 (2020).
- [33] C. Adamo and V. Barone, Toward reliable density functional methods without adjustable parameters: The PBE0 model, *J. Chem. Phys.* **110**, 6158 (1999).
- [34] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [35] Technically, this breaches ensemble theorems [11,12]. However, in BH and Be excluding the single excitation can be rigorously justified on point-group-symmetry grounds [28]. In CH<sub>2</sub> and nitroxyl it is less rigorously justifiable yet causes no apparent problems for self-consistency.
- [36] J.-D. Chai and M. Head-Gordon, Systematic optimization of long-range corrected hybrid density functionals, *J. Chem. Phys.* **128**, 084106 (2008).
- [37] A. D. Becke, A new mixing of Hartree-Fock and local density-functional theories, *J. Chem. Phys.* **98**, 1372 (1993).
- [38] J. F. Dobson and T. Gould, Calculation of dispersion energies, *J. Phys.: Condens. Matter* **24**, 073201 (2012).
- [39] X. Ren, P. Rinke, C. Joas, and M. Scheffler, Random-phase approximation and its applications in computational chemistry and materials science, *J. Mater. Sci.* **47**, 7447 (2012).
- [40] H. Eshuis, J. E. Bates, and F. Furche, Electron correlation methods based on the random phase approximation, *Theor. Chem. Acc.* **131**, 1 (2012).
- [41] A. Hesselmann, Intermolecular interaction energies from Kohn-Sham random phase approximation correlation methods, in *Non-covalent Interactions in Quantum Chemistry and Physics*, edited by A. O. de la Roza and G. A. DiLabio (Elsevier, 2017), Chap. 3, pp. 65–136.
- [42] G. P. Chen, V. K. Voora, M. M. Agee, S. G. Balasubramani, and F. Furche, Random-phase approximation methods, *Annu. Rev. Phys. Chem.* **68**, 421 (2017).
- [43] J. P. Perdew and Y. Wang, Accurate and simple analytic representation of the electron-gas correlation energy, *Phys. Rev. B* **45**, 13244 (1992).
- [44] K. Burke, A. Cancio, T. Gould, and S. Pittalis, Locality of correlation in density functional theory, *J. Chem. Phys.* **145**, 054112 (2016).
- [45] F. Furche, Molecular tests of the random phase approximation to the exchange-correlation energy functional, *Phys. Rev. B* **64**, 195120 (2001).
- [46] P. Mori-Sánchez, A. J. Cohen, and W. Yang, Failure of the random-phase-approximation correlation energy, *Phys. Rev. A* **85**, 042507 (2012).
- [47] T. Gould, A. Ruzsinszky, and J. P. Perdew, Simple self-interaction correction to random-phase-approximation-like correlation energies, *Phys. Rev. A* **100**, 022515 (2019).
- [48] A. Becke, A. Savin, and H. Stoll, Extension of the local-spin-density exchange-correlation approximation to multiplet states, *Theor. Chim. Acta* **91**, 147 (1995).
- [49] J. P. Perdew, A. Savin, and K. Burke, Escaping the symmetry dilemma through a pair-density interpretation of spin-density functional theory, *Phys. Rev. A* **51**, 4531 (1995).
- [50] G. L. Manni, R. K. Carlson, S. Luo, D. Ma, J. Olsen, D. G. Truhlar, and L. Gagliardi, Multiconfiguration pair-density functional theory, *J. Chem. Theory Comput.* **10**, 3669 (2014).
- [51] J. F. Stanton and R. J. Bartlett, The equation of motion coupled-cluster method. A systematic biorthogonal approach to molecular excitation energies, transition probabilities, and excited state properties, *J. Chem. Phys.* **98**, 7029 (1993).
- [52] H. Koch, O. Christiansen, P. Jørgensen, A. M. S. de Merás, and T. Helgaker, The CC3 model: An iterative coupled cluster approach including connected triples, *J. Chem. Phys.* **106**, 1808 (1997).
- [53] G. M. J. Barca, A. T. B. Gilbert, and P. M. W. Gill, Hartree-Fock description of excited states of H<sub>2</sub>, *J. Chem. Phys.* **141**, 111104 (2014).
- [54] M. Hellgren, F. Caruso, D. R. Rohr, X. Ren, A. Rubio, M. Scheffler, and P. Rinke, Static correlation and electron localization in molecular dimers from the self-consistent RPA and GW approximation, *Phys. Rev. B* **91**, 165110 (2015).
- [55] N. Colonna, M. Hellgren, and S. de Gironcoli, Molecular bonding with the RPAX: From weak dispersion forces to strong correlation, *Phys. Rev. B* **93**, 195108 (2016).
- [56] R. M. Parrish *et al.*, Psi4 1.1: An open-source electronic structure program emphasizing automation, advanced libraries, and interoperability, *J. Chem. Theory Comput.* **13**, 3185 (2017).
- [57] D. G. A. Smith *et al.*, Psi4numpy: An interactive quantum chemistry programming environment for reference implementations and rapid development, *J. Chem. Theory Comput.* **14**, 3504 (2018).
- [58] T. H. Dunning, Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen, *J. Chem. Phys.* **90**, 1007 (1989).
- [59] The degenerate case is more complicated as  $w = 1$  gives an ensemble over degenerate excitations; for the purpose of treating density-driven correlations we treat degenerate ensembles as though they are a single pure state.
- [60] F. Weigend and R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.* **7**, 3297 (2005).
- [61] A. Hellweg, C. Hättig, S. Höfener, and W. Klopper, Optimized accurate auxiliary basis sets for RI-MP2 and RI-CC2 calculations for the atoms Rb to Rn, *Theor. Chem. Acc.* **117**, 587 (2007).