On the Physical Origin of the 1/4 Exact Exchange in Density Functional Theory

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Exchange interactions are a manifestation of the quantum mechanical nature of the electrons, and play a key role in predicting the properties of materials from first principles. A widely used approximation to the exchange energy in density functional theory (DFT) combines 1/4 of Hartree-Fock (HF) with 3/4 of density-based exchange energies. This so-called hybrid DFT scheme is remarkably accurate, for reasons that are still poorly understood. Here we show that the 1/4 fraction of HF exchange is compatible with a correct quantum mechanical treatment of the exchange energy of an electron pair in the interacting electron gas, and that it mimics a correlation between doubly-excited electronic configurations that is not included in semilocal DFT. A consequence of our result is that 3/4 is the correct fraction of density-based exchange, even for an ideally accurate explicit exchange density functional. The relation between our results and trends observed in hybrid DFT calculations is discussed, along with other implications.

In the framework of density functional theory (DFT), the total energy can be expressed as a functional of the electron density [1], and minimized to obtain the ground state energy [2]. In practice, since the electron interactions cannot at present be expressed exactly in terms of the density, one needs to approximate the exchange and correlation energies, often using a local functional of the density, as is done in the local density approximation (LDA) and in the generalized gradient approximations (GGAs) of DFT [3, 4]. So-called hybrid exchange-correlation functionals [5] — a popular choice in modern DFT calculations — replace part of the density-based exchange energy with orbital-based Hartree-Fock (HF) (so-called “exact”) exchange, improving the accuracy of several computed properties.

In the simplest hybrid functional, called PBE0 [6–8], a single parameter $\alpha$ equal to the fraction of HF exchange is employed for the exchange mixing, according to $E_{XC} = E_{XC}^{\text{DFT}} + \alpha(E_{X}^{\text{HF}} - E_{X}^{\text{DFT}})$; here, $E_{X}$ and $E_{XC}$ are the exchange and exchange-correlation energies, respectively, and the DFT and HF superscripts denote density-based and HF-based quantities. It is well known [9, 10] that an exact-exchange fraction of roughly $\alpha = 1/4$ gives optimal ground state energies and properties, especially when used in conjunction with an accurate semilocal functional such as a GGA. Even in the more advanced range-separated HSE hybrid functional [11], which separates the short- and long-range parts of exchange, the optimal fraction of short-range exchange is 1/4. However, as Perdew put it [9], one should think of the 1/4 fraction as an empirical parameter, because a rigorous argument for it is still missing. There have been efforts to rationalize its physical origin [10] and understand why exact exchange mixing improves the ground state energy, but a rigorous physical explanation has not yet been proposed [9].

A hint about the role of exact exchange is offered by the $\alpha = 1$ limit (a unit fraction of exact exchange), which leads to inaccurate ground state energies except in the high-density limit, where correlation effects are negligible. This trend shows that electron correlations cannot be fully described by local interactions, and that mixing exact exchange is an attempt to account for missing correlation effects. Brillouin’s theorem [12], which states that in an orbital-based picture only doubly-excited configurations (and higher excitations) can contribute to the correlation energy, further indicates that mixing exact exchange may mimic correlation processes due to excited configurations.

Here we show that a hybrid functional with 1/4 exact exchange mixing mimics the correct quantum mechanical (QM) treatment of the exchange energy of an electron pair in the interacting electron gas of a material. The 1/4 exact exchange is associated with a spin-flip exchange interaction due to the coupling between doubly-excited configurations, which is missing in semilocal DFT. Comparing a classical statistical ensemble with a fully QM treatment of the electron spin, our approach shows that the 4 in the 1/4 fraction reflects the number of possible spin states of an electron pair. This work focuses on the hybrid DFT treatment of the ground state, and does not examine the problem of band gap calculations using hybrid DFT, which has been recently addressed [13, 14].

RESULTS

Exchange interactions. In its spirit, DFT is a classical theory of the electron gas. As Hohenberg and Kohn put it in their seminal work [1], in DFT “the system of electrons is pictured like a classical liquid” with electron density $n$. This statement has profound implications. The electron density $n(x)dv$, where $x = \{r, \sigma\}$ combines the position $r$ and spin $\sigma$ variables, is equal to the number of particles times the probability of finding a particle with spin $\sigma$ within the volume $dv$ around the point $r$ [15]. Therefore, DFT is a QM theory based on a real-valued probability — the electron density — rather than a complex-valued probability amplitude, as is the wave function. Here we will regard the treatment of a quantity as classical when it depends only on the density.
The main problem with an electronic structure theory based on probability is that exchange is an inherently QM interaction, since it is related to spin. Exchange interactions lower the electron repulsion energy by keeping a pair of electrons apart. In HF, a pairwise treatment of exchange is adopted, in which only particles occupying spin-orbitals with parallel spin contribute to the exchange energy. The density-based picture of DFT is pairwise, an accurate treatment of exchange needs a theory which, unlike DFT, explicitly treats two-particle correlations. The two-particle density matrix [15] is a natural extension of the electron density to treat two-body correlations. The electron repulsion energy of an electron pair, \( E_p \), can be written explicitly as a functional of its two-particle density matrix, \( \rho(x_1, x_2) \), using [15, 17]

\[
E_p = \int dx_1 dx_2 V_{12}(r_1, r_2) \rho(x_1, x_2),
\]

where \( V_{12} = \frac{e^2}{|r_1 - r_2|} \) is the two-body Coulomb interaction.

Focusing on the two doubly-occupied orbitals \( \phi_i \) and \( \phi_j \) defined above, and neglecting self-interaction, the only relevant exchange processes are those between electrons occupying the two different orbitals. We thus model a pair made up by an electron in orbital \( \phi_i \) with spin \( \sigma \) and an electron in orbital \( \phi_j \) with spin \( \sigma' \), and investigate its two-particle density matrix and contribution to exchange. We imagine measuring the spin of the two electrons composing the pair. Since the electron gas is unpolarized, we expect to measure one of these four outcomes with equal probability: spin up for both electrons, spin down for both electrons, spin up for the electron in orbital \( \phi_i \) and spin down for the electron in orbital \( \phi_j \), or vice versa. Given that electrons are indistinguishable, we express each of these four scenarios, respectively, with a two-particle Slater determinant formed with spin-orbitals \( \phi_{i\sigma} \) and \( \phi_{j\sigma'} \) and properly normalized:

\[
|\Psi_1\rangle \equiv |\uparrow\uparrow\rangle = \text{det}[\phi_{i\uparrow}, \phi_{j\uparrow}] \\
|\Psi_2\rangle \equiv |\downarrow\downarrow\rangle = \text{det}[\phi_{i\downarrow}, \phi_{j\downarrow}] \\
|\Psi_3\rangle \equiv |\uparrow\downarrow\rangle = \text{det}[\phi_{i\uparrow}, \phi_{j\downarrow}] \\
|\Psi_4\rangle \equiv |\downarrow\uparrow\rangle = \text{det}[\phi_{i\downarrow}, \phi_{j\uparrow}],
\]

Explicit expressions for these states are, for example,

\[
\Psi_1(x_1, x_2) = \frac{\phi_i(r_1)\phi_j(r_2) - \phi_j(r_1)\phi_i(r_2)}{\sqrt{2}} \times |00\rangle
\]

\[
\Psi_2(x_1, x_2) = \frac{\phi_i(r_1)\phi_j(r_2) - \phi_j(r_1)\phi_i(r_2)}{\sqrt{2}}(1) ,
\]

and similar ones for \( |\Psi_3\rangle \) and \( |\Psi_4\rangle \). Here and below, we adopt a convention commonly used in quantum information [18], in which \( |0\rangle \) and \( |1\rangle \) represent spin up and spin down states, respectively, and the tensor product \( |\sigma\sigma'\rangle = |\sigma\rangle \otimes |\sigma'\rangle \) is a spin state of the two electrons.

Using the states in Eq. (6) as a basis set, we formulate two models of the electron pair, both consistent with the spin measurements discussed above. The first approach, called here model 1, describes the pair with a wave function \( |\Psi_p\rangle \) consisting of an equal quantum superposition of the four states:

\[
|\Psi_p\rangle = \frac{1}{\sqrt{4}}(|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle + |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle).
\]
The corresponding two-particle density matrix, $\rho^{(1)}$, is a so-called pure state \[18\],

$$
\rho^{(1)} = |\Psi_p\rangle\langle\Psi_p| = \frac{1}{4} \sum_{\mu \nu = 1}^4 |\Psi_{\mu}\rangle\langle\Psi_{\nu}|.
$$

(9)

This description of the electron pair is the simplest ansatz that includes quantum superposition and two-body correlations.

We contrast this description of the pair with one based on probability alone, called here model 2, which does not use quantum superposition and is “classical” and similar in spirit to DFT. In model 2, the pair is described as a statistical ensemble composed in equal parts by the four pair basis states in Eq. (6). This model corresponds to a mixed state \[18\], generally described by the density matrix $\rho = \sum_{\mu} P_{\mu} |\Psi_{\mu}\rangle\langle\Psi_{\mu}|$. For our model 2, the two-particle density matrix is

$$
\rho^{(2)} = \frac{1}{4} \sum_{\mu = 1}^4 |\Psi_{\mu}\rangle\langle\Psi_{\mu}|,
$$

(10)

so that in our case, $P_{\mu} = 1/4$ is the probability of finding the electron pair in state $|\Psi_{\mu}\rangle$. The two models of the pair, and their associated density matrices $\rho^{(1)}$ and $\rho^{(2)}$, are represented schematically in Fig. 2. Note that spin measurements on the electron pair will give, both in model 1 and 2 (but for different reasons), one of the four states in Eq. (6) with equal probability of $1/4$, consistent with our assumption of an unpolarized electron gas.

An important property of $\rho^{(1)}$ and $\rho^{(2)}$ is that they are $N$-representable \[17\], in the sense that they can both be derived from two-body reduced density matrices, each obtained from an $N$-body density matrix by tracing out $N - 2$ electrons \[17\]. The $N$-representability guarantees that the energy derived using Eq. (5) is physically meaningful \[17\]; it further reveals the origin of $\rho^{(1)}$ and $\rho^{(2)}$ in terms of many-electron configurations. As we show in the Methods section, one can derive $\rho^{(1)}$ and $\rho^{(2)}$ from doubly-excited configurations described by Slater determinants in which an electron has been removed from each of the orbitals $\varphi_i$ and $\varphi_j$ and placed into unoccupied states [see Fig. 1(b)–(c)]. Due to Brillouin’s theorem, and as is known in configuration interaction theories, such doubly-excited configurations contribute to the ground state energy \[12, 19\].

Origin of the 1/4 exact exchange. To obtain the exchange energy of the electron pair in the two models, $E_X^{(i)}$ ($i = 1, 2$), we compute the matrix elements of the Coulomb interaction $V_{12}$ between the two-particle determinant basis states in Eq. (6):

$$
E_X^{(1)} = \text{Tr}[\rho^{(1)} V_{12}] = \frac{1}{4} \sum_{\mu \nu} \langle\Psi_{\mu}|V_{12}|\Psi_{\nu}\rangle = \frac{1}{4} \sum_{\mu \nu} M_{\mu \nu},
$$

$$
E_X^{(2)} = \text{Tr}[\rho^{(2)} V_{12}] = \frac{1}{4} \sum_{\mu} \langle\Psi_{\mu}|V_{12}|\Psi_{\mu}\rangle = \frac{1}{4} \sum_{\mu} M_{\mu \mu},
$$

(11)

where the sums run over the four basis states, and we define the exchange part of the matrix elements as

$$
M_{\mu \nu} = \langle\Psi_{\mu}|V_{12}|\Psi_{\nu}\rangle_X,
$$

(12)

where the subscript $X$ denotes that only the exchange integrals are kept. With these definitions, the exchange matrix $M$ becomes (see Methods):

$$
M = \begin{pmatrix}
J & 0 & 0 & 0 \\
0 & J & 0 & 0 \\
0 & 0 & 0 & J \\
0 & 0 & J & 0
\end{pmatrix}.
$$

(13)

The only nonzero off-diagonal matrix element is $M_{34} = \langle\uparrow \downarrow |V_{12}| \downarrow \uparrow\rangle_X = J$ (and $M_{33} = M_{44}$), which corresponds to a spin-flip exchange interaction (see Fig. 3) between pair states with antiparallel spins in the orbitals $\varphi_i$ and $\varphi_j$. This interaction contributes to the exchange energy only in model 1 [see Eq. (11)], and is associated with an exchange process between two doubly-excited configurations in which an electron in spin-orbital $\varphi_{j \uparrow}$ scatters into $\varphi_{i \uparrow}$, while an electron in spin-orbital $\varphi_{i \downarrow}$ scatters into $\varphi_{j \downarrow}$, due to the Coulomb interaction (see Fig. 3). This interaction is not included in HF, it should be regarded as a correlation — in the guise of an exchange process — arising from the coupling between doubly-excited configurations that contribute to the ground state energy.

We argue below that such spin-flip exchange interactions, which are not included in the LDA or GGA exchange and correlation energies, are the origin of the 1/4 exact exchange missing in semilocal DFT.
The exchange energy of the pair in the two models is obtained from Eq. (11) with the matrix $M$ given above:

$$E_X^{(1)} = \sum_{\mu \nu} M_{\mu \nu} = J$$

$$E_X^{(2)} = \frac{1}{4} \sum_{\mu} M_{\mu \mu} = \frac{J}{2}.$$

Note that the QM treatment of model 1 accounts for all of the four processes contributing to exchange, including the parallel-spin exchange processes, $M_{11}$ and $M_{22}$, and the two spin-flip exchange process, $M_{34}$ and $M_{43}$. By contrast, the ensemble description of the pair in model 2 misses the two spin-flip exchange process $M_{34}$ and $M_{43}$.

Since model 1 is a proper QM treatment of the pair in the interacting electron gas, we rename $E_X^{(1)}$ to just $E_X$, the exchange energy of the electron pair, and write:

$$E_X = E_X^{(2)} + \frac{J}{2}. \quad (15)$$

As we noted above, the last term in Eq. (15) equals one quarter of the HF exchange energy contribution from the interaction between the two orbitals $\varphi_i$ and $\varphi_j$, so we can write:

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Origin of the 3/4 density-based exchange. Our next goal is to express $E_X^{(2)}$ in Eq. (16) in the density-based picture, which is natural since model 2 is a probability-based approach, similar to DFT. We show below that the exchange energy $E_X^{(2)}$ of the pair described as a statistical ensemble in model 2 corresponds to 3/4 of the density-based exchange energy, so that the exchange energy for a pair of occupied orbitals is

$$E_X = \frac{3}{4} E_{\text{DFT}} + \frac{1}{4} E_{\text{HF}}. \quad (17)$$

Comparing this result with Eq. (4) tells us that a hybrid functional with 1/4 mixing contains, for each pair of orbitals, the correct exchange interactions, which account for both the same-spin exchange and the spin-flip exchange from interacting doubly-excited configurations.

Expressing in terms of the density the exchange energy $E_X^{(2)}$ of an electron pair in model 2 requires shifting from a pairwise to a density-based view of exchange interactions. Model 2 is a statistical ensemble of the four possible spin states of the pair; within each state, the exchange interaction is described by the matrix element $M_{\mu \nu}$, where $\mu = 1, \ldots, 4$ labels the spin state of the electron pair. As we noted earlier, all particles in the electron density contribute the same exchange in semilocal DFT, regardless of their spin. This means that one can identify the fraction of electrons contributing to exchange, and then assign to all such electrons the same contribution, which is a functional of the total electron density.

If the electron gas is described as an ensemble of pairs using a probability-based treatment, only the pairs in the electron gas in a triplet state contribute to exchange due to their spatially antisymmetric wave function. In our model 2 of the electron pair, both $|\Psi_1\rangle = A_ij |00\rangle$ and $|\Psi_2\rangle = A_{ij} |11\rangle$ are spatially antisymmetric [see Eq. (7)] triplet states. However, the spatial parts of $|\Psi_3\rangle = |1\uparrow 0\downarrow\rangle$ and $|\Psi_4\rangle = |1\downarrow 0\uparrow\rangle$ lack a well-defined symmetry. The problem is clearer when shown in a pictorial view of the statistical ensemble $\rho^{(2)} = \sum_{\mu} |\Psi_\mu\rangle \langle \Psi_\mu|$, where the portions of the system in states $|\Psi_1\rangle$ and $|\Psi_2\rangle$ clearly contribute to exchange with their corresponding

FIG. 3. Feynman diagram (left) and schematic visualization (right) of the spin-flip exchange interaction $M_{34}$ coupling the states $|\Psi_3\rangle = |\uparrow \downarrow\rangle$ and $|\Psi_4\rangle = |\downarrow \uparrow\rangle$. This interaction can only occur between doubly-excited configurations in which the orbitals $\varphi_i$ and $\varphi_j$ are each occupied by only one electron.
matrix elements $M_{11} = M_{22} = J$, but it is unclear how the other half of the system, in states $|\Psi_3\rangle$ and $|\Psi_4\rangle$, contributes, since the spin-flip exchange process hides in the interaction $M_{34}$ between these two states.

This subtle issue can be resolved by diagonalizing $M$ in the subspace of states $|\Psi_3\rangle$ and $|\Psi_4\rangle$, which provides a singlet and a triplet state with well-defined spatial wave function symmetry. Such triplet state $|\Psi_T\rangle$ and singlet state $|\Psi_S\rangle$ can be written in terms of $|\Psi_3\rangle$ and $|\Psi_4\rangle$ as

$$|\Psi_T\rangle = \frac{1}{\sqrt{2}} (|\Psi_3\rangle + |\Psi_4\rangle) = A_{ij}(r_1, r_2) \times \left( \frac{|01\rangle + |10\rangle}{\sqrt{2}} \right)$$

$$|\Psi_S\rangle = \frac{1}{\sqrt{2}} (|\Psi_3\rangle - |\Psi_4\rangle) = S_{ij}(r_1, r_2) \times \left( \frac{|01\rangle - |10\rangle}{\sqrt{2}} \right)$$

(18)

where $A_{ij}(r_1, r_2) = |\varphi_i(r_1)r_j(r_2) - \varphi_j(r_1)r_i(r_2)|/\sqrt{2}$ is the antisymmetric spatial wave function used above, and $S_{ij}(r_1, r_2) = |\varphi_i(r_1)r_j(r_2) + \varphi_j(r_1)r_i(r_2)|/\sqrt{2}$ is a symmetric spatial wave function. It is clear that only $|\Psi_T\rangle$ contributes to exchange due to its antisymmetric spatial wave function, but $|\Psi_S\rangle$ does not.

The electron pair ensemble $\rho^{(2)}$ can be rewritten as formed for 3/4 by triplet $(|\Psi_1\rangle, |\Psi_2\rangle$ and $|\Psi_T\rangle$) and 1/4 by singlet $(|\Psi_S\rangle)$ spin states:

$$\rho^{(2)} = \frac{1}{4} \sum_{\mu=1}^4 |\Psi_\mu\rangle \langle \Psi_\mu|$$

$$= \frac{1}{4} \left( |\Psi_1\rangle \langle \Psi_1| + |\Psi_2\rangle \langle \Psi_2| + |\Psi_T\rangle \langle \Psi_T| + |\Psi_S\rangle \langle \Psi_S| \right).$$

(19)

This different way of expressing $\rho^{(2)}$, in terms of pair states with a well-defined total spin, is shown schematically in Fig. 4(b). The part of the ensemble contributing to exchange, which is called below $\rho^{(2)}_E$, contains the terms in $\rho^{(2)}$ proportional to $|A_{ij}(r_1, r_2)|^2$:

$$\rho^{(2)}_E = \frac{1}{4} \left( |\Psi_1\rangle \langle \Psi_1| + |\Psi_2\rangle \langle \Psi_2| + |\Psi_T\rangle \langle \Psi_T| \right).$$

(20)

We can thus show that the fraction of electrons $\alpha_E$ contributing to the density-based exchange equals 3/4:

$$\alpha_E = \frac{\int dx_1 n_E(x_1)}{\int dx_1 n(x_1)} = \frac{\int dx_1 dx_2 \rho^{(2)}_E(x_1, x_2)}{\int dx_1 dx_2 \rho^{(2)}(x_1, x_2)} = \frac{3}{4}.$$ 

(21)

Above, the electron density of the pair, $n(x)$, is obtained from the two-body density matrix as [15, 17]

$$n(x) = 2 \int dx_2 \rho^{(2)}(x, x_2)$$

(22)

$$= \frac{1}{2} \left[ |\varphi_1|^2(r) + |\varphi_2|^2(r) \right] \left( |0\rangle \langle 0| + |1\rangle \langle 1| \right),$$

which correctly integrates to 2 electrons, while the electron density contributing to exchange is

$$n_E(x) = 2 \int dx_2 \rho^{(2)}_E(x, x_2)$$

(23)

$$= \frac{1}{2} \left[ |\varphi_1|^2(r) + |\varphi_2|^2(r) \right] \times \frac{3}{4} \left( |0\rangle \langle 0| + |1\rangle \langle 1| \right),$$

which integrates to $2 \times \frac{3}{4}$ electrons. Since only the triplet states contribute to exchange, only a fraction of $\alpha_E = 3/4$ of each electron pair constituting the system should be included in the density-based exchange energy, and we can write $E^{(2)}_X = 3/4 E^{DFT}_X[n]$. This step concludes our proof of Eq. (17) and justifies Eq. (4) for the hybrid DFT exchange energy contributed by a pair of electron orbitals. After resolving some subtleties (see Methods), this result can be extended to the entire electron gas, explaining the origin of the 1/4 exchange mixing of hybrid DFT.
Systems with less than four electrons. We discuss numerical results that corroborate our interpretation of the origin of the 1/4 exact exchange, focusing on trends obtained with hybrid functionals in systems with less than four electrons. Our treatment of the physical origin of the 1/4 exact exchange is valid only when at least four electrons (in two doubly-occupied orbitals) are present, since otherwise 1/4 $E_{\text{HF}}^X$ does not equal the correlation processes due to doubly-excited configurations. Perdew et al. [10] compiled a table of atomization energies of several molecules, and showed that a simple PBE0 hybrid with 1/4 exact exchange dramatically improves the accuracy of the computed atomization energy compared to LDA calculations, in which atomization energies are significantly overestimated. The only three molecules in the data set with less than four electrons – H$_2$, Li$_2$, and LiH – are an exception to this trend [10]; their atomization energies computed with the hybrid functional exhibit nearly the same or a larger discrepancy with experiment than in the LDA. In Table I, we give for convenience the atomization energies of H$_2$, Li$_2$, and LiH from Ref. 10; they can be reproduced, with similar results, with any modern DFT package, as we have verified.

TABLE I. Atomization energies (in eV units) taken from Ref. [10] for molecules in which a hybrid with 1/4 exact exchange does not improve the accuracy of the LDA result.

| Material | LDA | 1/4 Hybrid | Experiment |
|----------|-----|------------|------------|
| H$_2$    | 113 | 105        | 109        |
| LiH      | 60  | 52         | 58         |
| Li$_2$   | 23  | 19         | 24         |

Note that these are the only three molecules in the data set with less than four valence electrons, and also the only molecules for which the hybrid result does not improve over the LDA. These trends indicate that the interpretation put forward in this work on the physical origin of the 1/4 exact exchange is consistent with hybrid DFT calculations, as we further discuss below.

DISCUSSION

While our derivations focused on the PBE0 hybrid functional, widely used range-separated hybrid functionals, such as the HSE [11], also employ a 1/4 fraction of exact exchange in their short-range exchange interactions. Since correlation interactions are typically short-ranged, the success of the HSE functional in predicting the ground state supports the result shown here that the 1/4 exact exchange mimics missing correlations.

While we focused on the unpolarized case, spin-polarized systems deserve further investigation. In the fully spin-polarized limit, spin measurements on any electron pair would return a triplet state with certainty, so our models 1 and 2 become equivalent and $\alpha = 0$ is optimal. We thus expect semilocal DFT to describe a simple ferromagnetic metal better than hybrid DFT with 1/4 mixing. This observation is consistent with hybrid DFT computations; for example, Paier et al. [20] compared the performance of PBE and HSE for Fe and other itinerant magnetic systems. In Fe, the magnetic moment using the PBE functional is in excellent agreement with experiment, while HSE makes large errors on the magnetic moment and exchange splitting [20].

Since DFT is a ground state approach, only ground state calculations should be used to assess the quality of an exchange-correlation functional. Yet, hybrid functionals are routinely employed to compute band gaps. Recent work [13, 14] has shown that the optimal mixing parameter $\alpha$ for the band gap is roughly equal to the inverse static dielectric constant, $\alpha \approx 1/\epsilon_\infty$, and is thus system dependent. Although hybrid functionals with $\alpha \approx 1/\epsilon_\infty$ mixing have also been used for structural properties [21], their use for ground state calculations is not rigorously justified. We argue that due to their nonlocal exchange hybrid functionals are flexible enough to mimic static screening for band gap and correlation for ground state calculations, for which a value of $\alpha \approx 1/4$ is appropriate in spin unpolarized systems.

It is known that in practice the optimal $\sim 1/4$ fraction of exact exchange examined here is appropriate when used in conjunction with GGA functionals (e.g., PBE or PW91), but not in general for mixing with the LDA exchange (although extensive tests for hybrid mixing with LDA are scarce). These trends in hybrid DFT calculations can be seen as a success of the GGAs, since their optimal exact exchange mixing is close to 1/4, a value we predict to be correct even for an ideal explicit exchange density functional.

The LDA and GGAs, with their unit fraction of local exchange, conflict with our finding that only a 3/4 fraction of density-based exchange should be used for a spin unpolarized system. We speculate that its unit fraction of density-based exchange may be responsible for LDA’s tendency to overbind in spite of its variational nature (LDA’s exchange and correlation energies derive, respectively, from a HF and a quantum Monte Carlo calculation of the HEG). Since $E_{\text{XC}}$ is dominated by exchange, the latter should be responsible for the overbinding of the LDA: if one were to include only a 3/4 fraction of density-based exchange (without adding a corresponding fraction of 1/4 exact exchange), then the LDA may well underbind and recover its variational character, but it would be inaccurate due to the lack of a complete exchange hole [22].

Finally, there is a vast literature on benchmarking hybrid functionals, but analyzing the technical intricacies of these tests on extensive data sets is beyond the scope of this work, which aims to make a conceptual advance. More work is needed to improve the treatment of exchange and correlation in DFT, but the hope is that the unconventional approach taken in this work will stimulate new ideas.
In summary, we have shown that a correct quantum mechanical treatment of an electron pair can explain the physical origin of the 1/4 exact exchange mixing in hybrid DFT. In a spin unpolarized system, the success of combining density- and orbital-based exchange is rationalized by analyzing separately the interactions due to triplet states in an ensemble treatment of the electron pair and the correlations due to coupled spin configurations in a quantum superposition (pure) state of the pair. Our interpretation that the 1/4 exact exchange mimics missing correlations and multireference character in semilocal DFT is consistent with observations from numerical hybrid DFT calculations.

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**METHODS**

\textbf{N-Representability of the Density Matrices} $\rho^{(1,2)}$.

Our definitions given above for $\rho^{(1)}$ and $\rho^{(2)}$ include only the terms in the reduced density matrices contributing to the exchange interaction between orbitals $\varphi_i$ and $\varphi_j$. In this section, we show that one can obtain $\rho^{(1)}$ from the 2-body reduced density matrix of a pure state $|\Psi_N^{(1)}\rangle \langle \Psi_N^{(1)}|$, with $|\Psi_N^{(1)}\rangle = \text{det}[\varphi_1, ..., \varphi_i|s|, ..., \varphi_j|s|, ....]$ a Slater determinant in which each electron occupying $\varphi_i$ and $\varphi_j$ is in the spin superposition state $|s\rangle = (|0\rangle + |1\rangle)/\sqrt{2}$ [see Fig. 1(b)]. Similarly, $\rho^{(2)}$ can be obtained as the equal-probability ensemble of four density matrices, $\Gamma_{\sigma\sigma'}$, each obtained from the 2-body reduced density matrix of a pure state $|\Psi_N^{(2)}\rangle \langle \Psi_N^{(2)}|$, with Slater determinant $|\Psi_N^{(2)}\rangle = \text{det}[\varphi_1, ..., \varphi_i|s|, ..., \varphi_j|s|, ....]$ [see Fig. 1(c)].

Following Lowdin [15], we define the 2-body reduced density matrix (2-RDM) $\Gamma(x_1, x_2)$ for $N$ electrons as

$$\Gamma(x_1, x_2) = \frac{1}{2} \int dx_3...dx_N |\Psi_N(x_1, x_2, x_3, ..., x_N)|^2$$

(24)

where $\Psi_N(x_1, x_2, x_3, ..., x_N)$ is an antisymmetric wave function for $N$ electrons, and $x = \{r, \sigma\}$ denotes both the spatial coordinate $r$ and the spin $\sigma$.

We specialize to the case in which the wave function $\Psi_N$ is a single Slater determinant, $\Psi_N = (1/\sqrt{N!}) \text{det}[\varphi_k]$, with $\{\varphi_k\}$ a set of orthonormal spin-orbitals labeled by the index $k = 1, ..., N$. In this case, the 2-RDM takes the simple form [22]

$$\Gamma(x_1, x_2) = \frac{1}{2} \left[ \gamma(x_1, x_1) \gamma(x_1, x_2) \right]$$

(25)

where $\gamma(x, x') = \sum_{k=1}^N \varphi_k^*(x) \varphi_k(x')$ is the 1-body density matrix. For a Slater determinant wave function, we can thus write the 2-RDM in Eq. (25) as

$$\Gamma(x_1, x_2) = \frac{1}{2} \left\{ \sum_{k=1}^N |\varphi_k(x_1)|^2 \right\} \left\{ \sum_{k'=1}^N |\varphi_{k'}(x_2)|^2 \right\}$$

(26)

$$- \sum_{k=1}^N \varphi_k^*(x_1) \varphi_k(x_2) \sum_{k'=1}^N \varphi_{k'}^*(x_2) \varphi_{k'}(x_1)$$

In our work, we focus on the contribution to exchange from an electron pair occupying two given spin-orbitals, $\varphi_i\sigma$ and $\varphi_j\sigma'$. We thus keep in the 2-RDM only the terms that involve these orbitals, and obtain the density matrix:

$$\Gamma(x_1, x_2) = \frac{1}{2} \{ [\varphi_i\sigma(x_1) \varphi_j\sigma'(x_2)]^2 + [\varphi_j\sigma'(x_1) \varphi_i\sigma(x_2)]^2 \}$$

(27)

where h.c. denotes the Hermitian conjugate of the previous term in brackets, and we removed the tilde to indicate we are no longer working with the full 2-RDM for $N$
electrons, but rather, with its two-electron part of relevance here. We write explicitly the spatial and spin parts, for each spin-orbital $\varphi_{i\sigma}(\mathbf{x})$ and its Hermitian conjugate $\varphi_{i\sigma}^*(\mathbf{x})$, as

$$
\varphi_{i\sigma}(\mathbf{x}) = \varphi_{i}(\mathbf{r})|\sigma\rangle
$$

$$
\varphi_{i\sigma}^*(\mathbf{x}) = \varphi_{i}^*(\mathbf{r})|\sigma\rangle.
$$

(28)

After substituting in Eq. (27), we obtain

$$
\Gamma_{\sigma\sigma'}(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{2} \left[ |\varphi_{1}(\mathbf{r}_1)|^2 |\varphi_{2}(\mathbf{r}_2)|^2 |\sigma\rangle\langle\sigma| - |\varphi_{1}(\mathbf{r}_1)|^2 |\varphi_{2}(\mathbf{r}_2)|^2 |\sigma\rangle\langle\sigma'| + |\varphi_{1}(\mathbf{r}_1)|^2 |\varphi_{2}(\mathbf{r}_2)|^2 |\sigma'|\langle\sigma| + h.c. \right].
$$

(29)

For given electron spins $\sigma$ and $\sigma'$, the density matrices $\Gamma_{\sigma\sigma'}$ correspond to the configurations in Fig. 1(c), of which we keep only the part contributing to exchange between the orbital $\varphi_i$ and $\varphi_j$. For same-spin electrons, $\Gamma_{\sigma\sigma'}$ takes a particularly simple form:

$$
\Gamma_{\uparrow\uparrow}(\mathbf{x}_1, \mathbf{x}_2) = |A_{ij}(\mathbf{r}_1, \mathbf{r}_2)|^2 |00\rangle\langle00|
$$

$$
\Gamma_{\downarrow\downarrow}(\mathbf{x}_1, \mathbf{x}_2) = |A_{ij}(\mathbf{r}_1, \mathbf{r}_2)|^2 |11\rangle\langle11|,
$$

(30)

where $A_{ij}(\mathbf{r}_1, \mathbf{r}_2) = |\varphi_{i}(\mathbf{r}_1)|\varphi_{j}(\mathbf{r}_2)| - |\varphi_{j}(\mathbf{r}_1)|\varphi_{i}(\mathbf{r}_2)|/\sqrt{2}$ is the antisymmetric spatial wave function defined above. We also see that $\Gamma_{\uparrow\uparrow} + \Gamma_{\downarrow\downarrow} = |\Psi_1\rangle\langle\Psi_1| + |\Psi_2\rangle\langle\Psi_2|$. The opposite-spin 2-RDMs can be combined to give:

$$
(\Gamma_{\uparrow\downarrow} + \Gamma_{\downarrow\uparrow})(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{2} \left[ |\varphi_{i}(\mathbf{r}_1)|^2 |\varphi_{j}(\mathbf{r}_2)|^2 |10\rangle\langle01| - |\varphi_{j}(\mathbf{r}_1)|^2 |\varphi_{i}(\mathbf{r}_2)|^2 |10\rangle\langle01| \right],
$$

(31)

so that $\Gamma_{\uparrow\downarrow} + \Gamma_{\downarrow\uparrow} = |\Psi_3\rangle\langle\Psi_3| + |\Psi_4\rangle\langle\Psi_4|$. Using these relations, the ensemble density matrix $\rho^{(2)}$ for model 2 defined in the main text can be rewritten as

$$
\rho^{(2)}(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{4} \left[ \Gamma_{\uparrow\uparrow} + \Gamma_{\downarrow\downarrow} + \Gamma_{\uparrow\downarrow} + \Gamma_{\downarrow\uparrow} \right].
$$

(32)

We have thus shown that $\rho^{(2)}$ is $N$-representable, since it can be expressed as an equal-weight ensemble of 2-RDMs for the four spin configurations in Fig. 1(c).

The density matrix $\rho^{(1)}$ for the pure state employed in model 1 can be obtained using a similar approach. In particular, we use the configuration in Fig. 1(b), in which the electrons in orbitals $\varphi_i$ and $\varphi_j$ are placed in the superposition spin state $|s\rangle = |0\rangle + |1\rangle)/\sqrt{2}$. Using the result in Eq. (29), and putting $|\sigma\rangle = |\sigma'\rangle = |s\rangle$, we obtain the 2-RDM

$$
\Gamma_{ss}(\mathbf{x}_1, \mathbf{x}_2) = |A_{ij}(\mathbf{r}_1, \mathbf{r}_2)|^2 |ss\rangle\langle ss|
$$

$$
= |A_{ij}(\mathbf{r}_1, \mathbf{r}_2)|^2 \times \frac{1}{4} \sum_{\sigma\sigma'\sigma''\sigma'''} |\sigma\sigma'\rangle\langle\sigma''\sigma'''|.
$$

(33)

Using Eq. (9), $\rho^{(1)} = \frac{1}{2} \sum_{\sigma_1,\sigma_2=\uparrow\downarrow} |\Psi_\sigma\rangle\langle\Psi_\sigma|$, together with the definitions of the states $|\Psi_\sigma\rangle$ in Eq. (6), one can show easily that $\rho^{(1)} = \Gamma_{ss}$. We conclude that $\rho^{(1)}$ derives from the 2-RDM for the configuration in Fig. 1(b).

**Exchange matrix derivation.** Let us discuss briefly how the exchange interaction matrix in Eq. (13) is obtained. The non-zero diagonal matrix elements are $M_{11} = M_{22} = J$, while $M_{33} = M_{44} = 0$ since for these matrix elements the exchange integral vanishes. We take the orbitals $\varphi_i$ and $\varphi_j$ to be real, so that $M$ is symmetric, and obtain the off-diagonal part of $M$ using the properties of the matrix elements of the two-body operator $V_{12}$ between Slater determinants that differ by one or two spin-orbitals (see Ref. 16). For example, $M_{12} = \langle \uparrow\uparrow | V_{12} | \downarrow\downarrow \rangle \chi$ is a matrix element taken between determinants differing by two spin-orbitals; it vanishes since no term survives the integration over spin. All of the $M_{13}, M_{14}, M_{23}, M_{24}$ also vanish since they are matrix elements between two determinants differing by one spin-orbital, which can be obtained from one another by flipping one spin.

**Exchange mixing in the entire electron gas.** We first discuss an important detail in comparing Eq. (4) and Eq. (17). In the former, $E_{\text{hybrid}}^{\text{X}}$ is computed using the electron density for doubly-occupied orbitals $\varphi_i$ and $\varphi_j$, which is due to four electrons, while in Eq. (17) the electron density integrates to two electrons. This subtlety can be resolved by observing that for the spin-flip exchange interaction to occur, only two electrons (one per orbital) can occupy the orbitals $\varphi_i$ and $\varphi_j$, since the initial and final states possess opposite spins in each orbital [see Fig. 3]. Therefore, to extend Eq. (17) to four electrons, one needs to use the density $n(\mathbf{r}) = 2(|\varphi_i(\mathbf{r})|^2 + |\varphi_j(\mathbf{r})|^2)$ for four electrons in the $3/4 E_{\text{X}}^{\text{DFT}}[n]$ term, as in Eq. (4), while keeping the spin-flip interaction as the one due to two electrons, which equals $1/4 E_{\text{X}}^{\text{HF}}$, since this term derives from doubly-excited configurations. After this step, our result in Eq. (17) matches exactly the hybrid DFT result in Eq. (4) we aim to explain. This reasoning provides the basis for extending the result to the entire electron gas. Using the density due to all occupied orbitals, and summing over all orbital pairs the pairwise part accounting for the spin-flip (exact) exchange, one obtains the total exchange energy for all the electrons in a hybrid functional with 1/4 mixing, $E_{\text{X}} = 3/4 E_{\text{X}}^{\text{DFT}}[n] + 1/4 E_{\text{X}}^{\text{HF}}$. Our results can thus rationalize, both for each pair of occupied orbitals and for the entire electron gas, the 1/4 exact exchange employed in hybrid DFT.
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