Kohn-Sham density functional theory (DFT) replaces the correlated wavefunction problem by a more tractable problem of non-interacting electrons moving in self-consistent effective potentials $V^\sigma(r)$ ($\sigma = \uparrow, \downarrow$) which generate the spin densities $n_\sigma(r)$ of the real (interacting) system. Exact in principle for the ground-state energy and density, Kohn-Sham DFT requires in practice an approximation for the exchange-correlation (xc) energy functional $E_{xc}[n_\uparrow, n_\downarrow]$. With improving approximations, DFT has become the standard method for electronic structure calculations in physics and chemistry.

In terms of the total electron density $n = n_\uparrow + n_\downarrow$ and exchange-correlation energy per electron $\epsilon_{xc}(r)$, we write

$$E_{xc} = \int dr n(r)\epsilon_{xc}(r).$$  

A ladder of approximations constructs $\epsilon_{xc}(r)$ as a function of density-dependent ingredients. The first three rungs are semi-local (with $\epsilon_{xc}$ found from the Kohn-Sham orbitals in an infinitesimal neighborhood of $r$) and in some versions non-empirical. The rungs are defined by the ingredients: (i) the local spin-density (LSD) approximation $E_{xc}^L$, which uses only $n_\sigma(r)$; (ii) the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) version, which adds the gradients $\nabla n_\sigma(r)$; (iii) the meta-GGA in the Tao-Perdew-Staroverov-Scuseria (TPSS) version, which further adds the positive orbital kinetic energy densities $\tau_\sigma(r)$; (iv) functionals employing a truly nonlocal ingredient, the exact (ex) exchange energy density $n_{xc}^{ex}$, either in full $E_{xc}^{ex}$ or in part $E_{xc}^{sl}$ or in part $E_{xc}^{hs}$. The currently used fourth-rung functionals are global hybrids (gh) mixtures of exact exchange and semi-local (sl) approximations

$$E_{xc}^{gh} = aE_{xc}^{ex} + (1 - a)E_{xc}^{sl} + E_{xc}^{hs},$$

where the exact-exchange mixing coefficient “$a$” is a global empirical parameter (typically $a \approx 0.2$). A global hybrid with $0 \leq a < 1$ does not satisfy any universal constraints beyond those satisfied by $E_{xc}^{ex}$.

In many real systems, these existing functionals are reasonably accurate for $E_{xc}$ and more accurate (due to error cancellation) for $E_{xc}$, with accuracy generally increasing up the ladder. Yet serious errors occur in nearly-separated open systems with fluctuating electron numbers that may not average to integer values, as summarized below. (a) In the dissociation of heteronuclear diatomics such as NaCl with bond length $R$, spurious fractional-charge $R \to \infty$ limits are common (e.g., Na$^{+0.4} \cdots$Cl$^{-0.4}$ instead of Na$^{0} \cdots$Cl$^{0}$), as are related charge-transfer errors. (In this example, Na$^+$Cl is a closed system of fixed integer electron number, while Na and Cl are separated open subsystems free to exchange electrons with each other). (b) In the dissociation of molecular radical cations $A^+_2$, the $R \to \infty$ limit is correctly $A^+_5 \cdots A^+_5$, but the total energy is far below that of $A^+_5 \cdot A^+_5$, with which it should be degenerate. For the one-electron molecule H$_2^+$, this is unambiguously a self-interaction error. The errors (a) and (b) are not necessarily corrected by functionals that are exact for all one-electron densities. (c) In the solid state, energy competition among electronic configurations in transition metal oxides, lanthanides, and actinides can be poorly described. These errors are similar in LSD, PBE, and TPSS, but are improved by global hybrids. In this Report, we derive the generalized x-hole sum rule and then explain at the most fundamental level why semi-local functionals fail for open systems by showing that they violate this rule. We also show that the errors of semi-local functionals for $E_{xc}$ can be corrected by a properly designed local hybrid functional.

For closed systems of integer electron number and integer occupation numbers, the exact (Hartree-Fock-like) exchange energy per electron at $r$ is given by

$$\epsilon_x(r) = \frac{1}{2} \int dr' \frac{n_x(r, r')}{|r - r'|},$$

where $n_x(r, r')$ is the density at $r'$ of the exchange hole.
around an electron at \( \mathbf{r} \):

\[
\rho_\sigma(\mathbf{r}, \mathbf{r}') = -\sum_\alpha \frac{|f_{\alpha\sigma}(\mathbf{r}, \mathbf{r}')|^2}{n(\mathbf{r})},
\]

in which

\[
\rho_\sigma(\mathbf{r}, \mathbf{r}') = \sum_\alpha f_{\alpha\sigma} \psi_{\alpha\sigma}(\mathbf{r}') \psi_{\alpha\sigma}(\mathbf{r})
\]

is the one-particle density matrix for spin \( \sigma \) of the Kohn-Sham non-interacting system, \( \psi_{\alpha\sigma} \) are orbitals and \( f_{\alpha\sigma} \) their occupation numbers (\( f_{\alpha\sigma} = 1 \) or 0). The density for spin \( \sigma \) is \( n_\sigma(\mathbf{r}) = \rho_\sigma(\mathbf{r}, \mathbf{r}) \).

A little-known aspect of the work of Perdew and Zunger \[13\] is their guess that Eqs. (3)–(5) apply, with fractional occupations \( 0 \leq f_{\alpha\sigma} \leq 1 \), even to an open subsystem (with average electron number \( \sum_\alpha f_{\alpha\sigma} = N \)) of a closed system. We confirm this guess numerically now and analytically later. Numerically, we find \[14\] that the total Hartree-Fock energy computed self-consistently by Eqs. (3)–(5) for a molecule \( \text{A}_2^+ \) at \( R \to \infty \) is exactly twice that of \( \text{A}^{+0.5} \). (The difference between Hartree-Fock and exact exchange-only DFT energies is unimportant on the scale of the effects we study).

Consider the total energy of an F atom, treated as an open system, as a function of average electron number \( N \). We vary \( N \) by changing the population of the highest partly-occupied 2p-orbital and compute the energy self-consistently using the GAUSSIAN program \[16\]. Fig. 1 shows that the total energy with exact exchange-correlation varies linearly between adjacent integers \[13, 17\], but the PBEx and PBExc energies curve upward strongly, while the HF energy curves downward. Note also the accuracy of PBExc energy differences for integer values of \( N \) around 9 and their inaccuracy for non-integer values. LSD \[17\], TPSS \[14\], and other functionals \[18\] behave similarly.

In Fig. 1, the Hartree-Fock approximation (exact exchange without correlation) shows substantial midpoint error for non-integer electron numbers. However, this error is positive and thus not very harmful since energy minimization forces integer electronic numbers onto separated open subsystems, e.g., a symmetry-broken \( \text{F} \cdot \cdot \cdot \text{F}^+ \) as the dissociation limit of \( \text{F}_2^+ \). But \( \text{F}^{+0.5} \cdot \cdot \cdot \text{F}^{+0.5} \) is a harmfully too-deep minimum for the semi-local density functionals, since their midpoint error is negative.

The failure of semi-local exchange can occur even in open systems with integer average electron number. In semi-local DFT, the correct dissociation limit for neutral homonuclear diatomics built up from open-shell atoms (e.g., \( \text{H}_2 \)) is achieved by spin symmetry breaking. If, however, spin symmetry is imposed, then the semi-local exchange energy in the \( R \to \infty \) limit is much more negative than the exact exchange energy \[19\]. Typically, the separated atoms have half-integer numbers of electrons of each spin (e.g., \( N_\uparrow = N_\downarrow = \frac{1}{2} \) on each spin-unpolarized H atom). But the \( \text{C}_2 \) molecule in the unusual singlet configuration \( KK^{(\sigma_22s)^2(\sigma_22s)^2(\pi_u2p_x)^2(\pi_u2p_y)^2} \) dissociates to two neutral C atoms, each with \( N_\uparrow = N_\downarrow = 3 \) but fractional occupations \( f_{2p_x\uparrow} = f_{2p_y\uparrow} = f_{2p_x\downarrow} = f_{2p_y\downarrow} = \frac{1}{2} \). Fig. 2 shows that, again, the spin-restricted semi-local exchange energy in the \( R \to \infty \) limit is far more negative than that of spin-restricted Hartree-Fock theory.

In a transition-state complex of a chemical reaction, residual fluctuation of electrons among its weakly-bonded fragments raises the total energy via increased Coulomb repulsion, but semi-local exchange approximations miss this effect and predict reaction barriers that are too low.

When we apply single-configuration Hartree-Fock theory to a closed system, fractional occupation numbers on
a separated open subsystem can only represent fluctuation of electrons among separated subsystems. That is the case we address here. In a different case, fractional occupation on a closed system can represent fluctuation of electrons among degenerate orbitals of that system.

We will now prove that Eqs. (3)–(5) apply to an open system of fluctuating electron number and then show how they imply the behavior found in Figs. 1 and 2. Let S be a fully separated open system and R its reservoir, i.e., the only other open system with which S is free to exchange electrons. Consider now the closed system S+R of integer electron number, which we will describe by a single Slater determinant. If the wavefunction of S+R were fully correlated, the ensemble describing S as a subsystem of S+R would also be 17, but since the former is only a single energy-minimized Slater determinant, the latter consists of Slater determinants and their probabilities that need not be energy-minimized. When we form S+R, each orthonormal orbital on S remains unchanged if there is no orbital of the same energy from R, or hybridizes (forms a linear combination) with orbitals of the same energy from R, resulting in a band whose width tends to zero in the infinite-separation limit (i.e., a group of nearly degenerate molecular orbitals). If this band is filled, hybridization is just a unitary transformation of the occupied orbitals. The Hartree-Fock exchange energy of S+R, as predicted by Eqs. (3)–(4), is a sum of a pure S term (arising when r and r' are on S) and a pure R term (arising when r and r' are on R), because when r is in S and r' in R the Coulomb interaction 1/|r−r'| vanishes. Thus, the S term is given by Eqs. (3)–(5) in which ψ_{ασ} are the orthonormal orbitals of S with f_{ασ} = 1 if the corresponding band is filled and 0 < f_{ασ} < 1 if it is partly filled (holds more nearly-degenerate orbitals than electrons), as it can be if the Fermi level lies within the band. This concludes the proof.

Now we can use the ensemble describing S to explain why the Hartree-Fock energy as a function of N curves downward. Let E_{HF}^S(S;S+R) be the Hartree-Fock energy of the N_e-electron pure state i of system S, evaluated from orbitals for S formed by truncating and renormalizing the ground-state molecular orbitals of S+R, and let p_i be the probability to find state i in the ground state of S+R, with \sum_i p_i = 1 and \sum_i N_i = N. Then E_{HF}^S(S;S+R) = \sum_i p_i E_{HF}^S(S;S+R) > \sum_i p_i E_{HF}^S(S;S). A familiar and instructive example 20 is the H atom in a spin-restricted stretched H_2 molecule, where the states i are the neutral atoms of each spin (p_{i/2} = 0.25, N_i = 1), cation (p_{i/2} = 0.25, N_i = 0), and anion (p_{i/2} = 0.25, N_i = 2). Another example 21 is Fig. 1 where the states i are those for N_i = J and J−1 electrons, with J an integer.

The reason why semi-local functionals predict too-negative energies for systems with fractional occupations also becomes clear. By the orthonormality of the orbitals of a subsystem, Eqs. (4) and (5) imply the sum rule

\[ \int dr' n_x(r',r') = -\sum_{α} \sum_{σ} f_{ασ} \frac{n_{ασ}(r')}{n(r)}. \]  

where \( n_{ασ}(r) = f_{ασ} |ψ_{ασ}(r)|^2 \). Eq. (6) for noninteger \( f_{ασ} \) was presented without proof in Ref. 13. Adding and subtracting \( -1 = -\sum_{ασ} n_{ασ}(r)/n(r) \) to Eq. (6), we find

\[ \int dr' n_x(r',r') = -1 + \sum_{ασ} f_{ασ}(1 - f_{ασ}) \frac{|ψ_{ασ}(r')|^2}{n(r)}. \]  

The close similarity between the sum rule integral [left-hand side of Eq. (7)] and the exchange-energy-per-electron integral [right-hand side of Eq. (3)] for integer \( f_{ασ} \) was pointed out by Gunnarsson and Lundqvist 22, and this similarity persists for noninteger values of \( f_{ασ} \). When all the occupation numbers are 1 or 0, the right-hand side of Eq. (7) becomes \(-1 \), which is also the sum rule implicitly assumed by LSD, PBE, and TPSS 23. But, when some occupation numbers are between 1 and 0, the right-hand side of Eq. (7) will fall between \(-1 \) and 0, meaning that part of the exact exchange hole around an electron in an open system is located in its distant reservoir. In this case a semi-local exchange approximation \( ε_{xc}^{\text{sl}} \) will tend to be more negative than the exact exchange energy per electron \( ε_{xc}^{\text{ex}}(r) \), as illustrated in Figs. 1 and 2. The total or system-averaged \( E_{xc}^{\text{sl}} \) also violates the sum rule on the system-averaged 24 x-hole

\[ \frac{1}{N} \int dr dr' n_x(r,r') = -1 + \frac{1}{N} \sum_{ασ} f_{ασ}(1 - f_{ασ}). \]  

The Hartree-Fock mean square fluctuation of electron number \( \sum_{ασ} f_{ασ}(1 - f_{ασ}) \), only vanishes when all occupations are 0 or 1.

A sum rule for the exact xc-hole density \( n_{xc}(r,r') \) is also known 17. Its integral equals \(-1 \) only when the electron number does not fluctuate and otherwise falls between \(-1 \) and 0. Ref. 17 presents a coupling-constant integration for \( E_{xc} \) and \( n_{xc} \). But the integral for \( E_{xc} \) at zero coupling strength is not really the exact exchange-only energy because of an exact-degeneracy static correlation. When the electron number on the infinitely-separated open system S fluctuates at the Hartree-Fock level, occupied and unoccupied orbitals (with the same spin) of closed system S+R are degenerate. Degenerate perturbation theory is needed to find the correlation energy, which is of the same order as the exchange energy even in the weak-coupling or high-density limits. Exact-degeneracy correlation and normal correlation shift the downward-curved Hartree-Fock energy of Fig. 1 into the straight-line correlated exact energy. Note also from Fig. 1 that semi-local approximations for \( E_{xc} \) overestimate the strength of exact-degeneracy correlation (which they introduce via \( E_{xc}^{\text{sl}} \)).

Semi-local functionals are often combined with a Hubbard U parameter (DFT+U). A simple case occurs when only one localized orbital has non-integer occupation \( f \), and the method adds to the semi-local energy a positive term \( U_f(1 - f) \). The close connection between DFT+U and self-interaction correction has been argued 25. We note that \( U \) does not represent “strong correlation” (as sometimes asserted), because the \( U \) needed to reach the
Hartree-Fock energy is greater than that needed to reach the exact correlated energy. $U$ favors the less fluctuating configuration by penalizing the more fluctuating one.

Our Fig. 1 and our analysis explaining it show that some region-dependent fraction (between 0 and 1) of exact exchange is needed to correct semi-local exchange-correlation approximations. Such a mixing of the downward-curving exact exchange with the upward-curving semi-local exchange and semi-local correlation can produce the needed straight line. This motivates a local hybrid (lh) functional

$$c_{\text{ex}}^{\text{lh}}(r) = c_{\text{ex}}^\text{sl} + [1 - a(r)](c_{\text{ex}}^\text{sl} - c_{\text{ex}}^\text{sl}) + c_{\text{ex}}^\text{sl},$$

where $0 \leq a(r) \leq 1$ and $\text{sl}=$TPSS. Eq. (9) was presented in Ref. 26 without a form for $a(r)$. Forms were proposed in Ref. 27 and in Ref. 7 (where the term “local hybrid” was coined), but did not achieve useful accuracy for equilibrium electron number, semi-local functionals overcorrelate and need a large positive correction, i.e., a large $a(r)$.

The Perdew-Zunger self-interaction correction [11] to semi-local functionals works in much the same way to raise the energy of a system with fractional occupation [11], satisfying the sum rule of Eq. (7). However, it loses the error cancellation between semi-local exchange and semi-local correlation in normal regions, and so is inaccurate for molecules near equilibrium geometries [28].

In summary, striking and diverse failures of semi-local functionals arise because they assign too low an energy to configurations where the electron number in a spin-polarized region fluctuates too strongly (i.e., where $c_{\text{ex}}^\text{sl}/c_{\text{ex}}^\text{sl} \ll 1$) at the Hartree-Fock level. These errors should be corrected by local mixing of a variable fraction of exact exchange.

A natural generalization of the global hybrid of Eq. (2), Eq. (9) can satisfy [3,27] many more exact constraints while achieving greater accuracy. We have developed and are testing [27] such a local hybrid hyper-GGA, and the results will be reported later. One or more universal empirical parameters are needed, as in Eq. (2), since the universal constraints are already satisfied by $a(r) = 1$. As usual, symmetry must be allowed to break. Spin-symmetry breaking [28], like real correlation, lowers the energy by suppressing Hartree-Fock-level fluctuation of electron number. Semi-local functionals mimic this suppression. Where real correlation cannot fully suppress fluctuation, as in open systems of non-integer average electron number, semi-local functionals overcorrelate and need a large positive correction, i.e., a large $a(r)$.

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