

## Exchange and correlation in open systems of fluctuating electron number

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While the exact total energy of a separated open system varies linearly as a function of average electron number between adjacent integers, the energy predicted by semilocal density-functional approximations is concave up and the exact-exchange-only or Hartree-Fock energy is concave down. As a result, semilocal density functionals fail for separated open systems of fluctuating electron number, as in stretched molecular ions  $A_2^+$  and in solid transition-metal oxides. We develop an exact-exchange theory and an exchange-hole sum rule that explain these failures and we propose a way to correct them via a local hybrid functional.

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Kohn-Sham density-functional theory [1,2] (DFT) replaces the correlated wave-function problem by a more tractable problem of noninteracting electrons moving in self-consistent effective potentials  $v_s^\sigma(\mathbf{r})$  ( $\sigma = \uparrow, \downarrow$ ) which generate the spin densities  $n_\sigma(\mathbf{r})$  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  $E_{xc}[n_\uparrow, n_\downarrow]$ . Then  $v_{xc}^\sigma(\mathbf{r}) = \delta E_{xc} / \delta n_\sigma(\mathbf{r})$ . 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  $\epsilon_{xc}(\mathbf{r})$ , we write

$$E_{xc} = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}(\mathbf{r}). \quad (1)$$

A ladder [3] of approximations constructs  $\epsilon_{xc}(\mathbf{r})$  as a function of density-dependent ingredients. As more ingredients are employed, they can be used to satisfy more exact constraints on  $E_{xc}$  and/or better fit experimental data. The first three rungs are semilocal (with  $\epsilon_{xc}$  found from the Kohn-Sham orbitals in an infinitesimal neighborhood of  $\mathbf{r}$ ) and in some versions nonempirical. The rungs are defined by the ingredients: (i) the local spin-density (LSD) approximation [1], which uses only  $n_\sigma(\mathbf{r})$ ; (ii) the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) [4] version, which adds the gradients  $\nabla n_\sigma(\mathbf{r})$ ; (iii) the meta-GGA in the Tao-Perdew-Staroverov-Scuseria (TPSS) [5] version, which further adds the positive orbital kinetic energy densities  $\tau_\sigma(\mathbf{r})$ ; (iv) functionals employing a truly nonlocal ingredient, the exact (ex) exchange energy density  $n\epsilon_x^{\text{ex}}$ , either in full [3,6] or in part [7,8]. The currently used fourth-rung functionals are global hybrids (gh) [9], mixtures of exact exchange and semilocal (sl) approximations

$$E_{xc}^{\text{gh}} = aE_x^{\text{ex}} + (1-a)E_x^{\text{sl}} + E_c^{\text{sl}}, \quad (2)$$

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  $E_x^{\text{sl}}$ .

In many real systems, these existing functionals are reasonably accurate for  $E_x$  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  $R \rightarrow \infty$  limits are common (e.g.,  $\text{Na}^{0.4+} \cdots \text{Cl}^{0.4-}$  instead of  $\text{Na}^0 \cdots \text{Cl}^0$ ), as are related charge-transfer errors. (In this example,  $\text{Na} \cdots \text{Cl}$  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  $R \rightarrow \infty$  limit is correctly  $A^{0.5+} \cdots A^{0.5+}$ , but the total energy is far below that of  $A \cdots A^+$ , with which it should be degenerate. For the one-electron molecule  $\text{H}_2^+$ , this is unambiguously [10] a self-interaction error. The errors (a) and (b) are not necessarily corrected by functionals that are exact for all one-electron densities [11]. (c) In the solid state, energy competition among electronic configurations in transition-metal oxides, lanthanides, and actinides can be poorly described [12]. These errors are similar in LSD, PBE, and TPSS, but are improved by global hybrids [12]. In this paper, we derive the generalized exchange-hole sum rule and then explain at the most fundamental level why semilocal functionals fail for open systems by showing that they violate this rule. We also show that the errors of semilocal 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-type) exchange energy per electron at  $\mathbf{r}$  is given by

$$\epsilon_x^{\text{ex}}(\mathbf{r}) = \frac{1}{2} \int d\mathbf{r}' \frac{n_x(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (3)$$

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

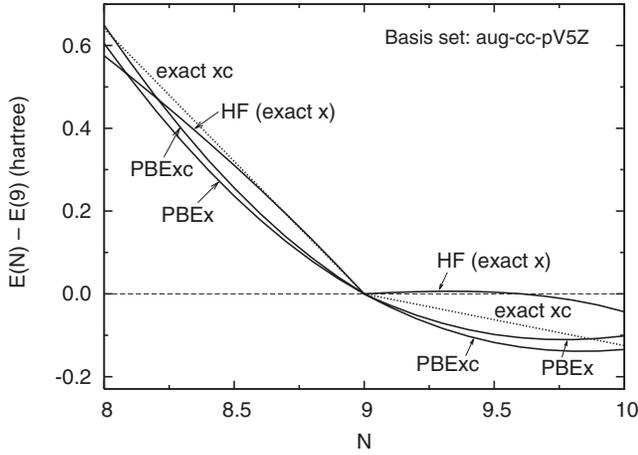


FIG. 1. Total energies of the F atom as functions of the average electron number  $N$  in the PBE approximation (with and without correlation) and in Hartree-Fock theory. The dotted lines represent the exact-xc result based on the experimental ionization potential and electron affinity of the F atom [16].

$$n_x(\mathbf{r}, \mathbf{r}') = - \sum_{\sigma} \frac{|\rho_{\sigma}(\mathbf{r}, \mathbf{r}')|^2}{n(\mathbf{r})}, \quad (4)$$

in which

$$\rho_{\sigma}(\mathbf{r}, \mathbf{r}') = \sum_{\alpha} f_{\alpha\sigma} \psi_{\alpha\sigma}(\mathbf{r}) \psi_{\alpha\sigma}^*(\mathbf{r}') \quad (5)$$

is the one-particle density matrix for spin  $\sigma$  of the Kohn-Sham system,  $\psi_{\alpha\sigma}$  are orbitals and  $f_{\alpha\sigma}$  their occupation numbers ( $f_{\alpha\sigma}=1$  or 0 for orbital energies below or above the Fermi level, respectively). 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  $N = \sum_{\alpha\sigma} f_{\alpha\sigma}$ ) 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  $A_2^+$  at  $R \rightarrow \infty$  is exactly 2 times that of  $A^{0.5+}$ . (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 [15]. Figure 1 shows that the total energy with exact exchange-correlation varies linearly between adjacent integers [16,17], but the PBE (PBE exchange) and PBExc (PBE exchange-correlation) energies are concave up strongly, while the HF energy is concave down. Note also the accuracy of PBExc energy differences for integer values of  $N$  around 9 and their inaccuracy for noninteger 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 noninteger electron numbers. However, this error is posi-

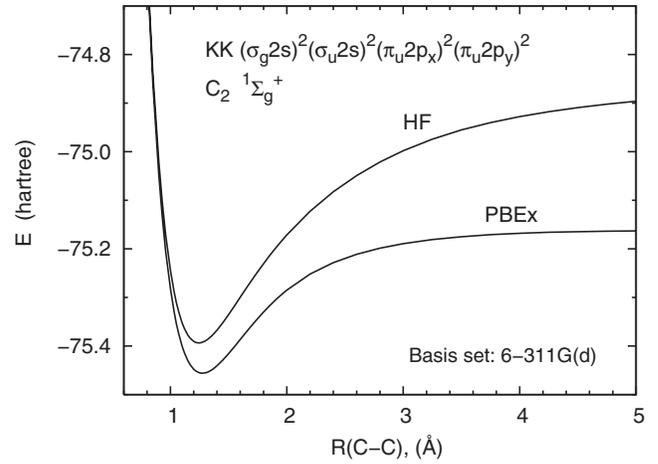


FIG. 2. Spin-restricted exchange-only dissociation curves for the  $C_2$  molecule in the unusual symmetric singlet electron configuration. This configuration is the lowest-energy state in the PBE approximation near the equilibrium internuclear distance but not at larger  $R$ , and not at any  $R$  in Hartree-Fock.

tive and thus not very harmful since energy minimization forces integer electron numbers onto separated open subsystems, e.g., a symmetry-broken  $F \cdots F^+$  as the dissociation limit of  $F_2^+$ . But  $F^{0.5+} \cdots F^{0.5+}$  is a harmfully too-deep minimum for the semilocal density functionals, since their midpoint error is negative.

The failure of semilocal exchange can occur even in open systems with integer average electron number. In semilocal DFT, the correct dissociation limit for neutral homonuclear diatomics built up from open-shell atoms (e.g.,  $H_2$ ) is achieved by spin symmetry breaking. If, however, spin symmetry is imposed, then the semilocal exchange energy in the  $R \rightarrow \infty$  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  $C_2$  molecule in the singlet configuration  $KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2$  dissociates to two neutral C atoms, each with  $N_{\uparrow} = N_{\downarrow} = 3$  but fractional occupations  $f_{2p_x\uparrow} = f_{2p_x\downarrow} = f_{2p_y\uparrow} = f_{2p_y\downarrow} = \frac{1}{2}$ . Figure 2 shows that, again, the spin-restricted semilocal exchange energy in the  $R \rightarrow \infty$  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 semilocal 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 infinitely distant reservoir. Consider now the closed system  $S+R$  of integer electron number, which we will describe by a single Slater determinant. Typically no more than one orbital of  $S$  can be fractionally occupied, say, the orbital  $\psi_S(\mathbf{r})$ . From the pair of normalized molecular orbitals  $\psi_S(\mathbf{r})$  and  $\psi_R(\mathbf{r})$ , where  $\psi_R(\mathbf{r})$  is the orbital of  $R$  most strongly mixed with  $\psi_S(\mathbf{r})$  at large finite separation, we may form a pair of molecular orbitals for  $S+R$ :  $\psi_+(\mathbf{r})=c\psi_S(\mathbf{r})+d\psi_R(\mathbf{r})$  and  $\psi_-(\mathbf{r})=-d\psi_S(\mathbf{r})+c\psi_R(\mathbf{r})$ , where  $c$  and  $d$  are real with  $c^2 \leq 1$  and  $c^2+d^2=1$ . In the absence of degeneracy between  $\psi_S(\mathbf{r})$  and  $\psi_R(\mathbf{r})$ ,  $c$  will be 1. Now the pure- $S$  contribution of  $\psi_+(\mathbf{r})$  and  $\psi_-(\mathbf{r})$  to the noninteracting density matrix (5) of  $S+R$  is  $f_S\psi_S(\mathbf{r})\psi_S^*(\mathbf{r}')$ , where  $f_S$  is  $c^2$  when only  $\psi_+(\mathbf{r})$  is occupied or  $c^2+d^2=1$  when both  $\psi_+(\mathbf{r})$  and  $\psi_-(\mathbf{r})$  are occupied. In  $E_x^{\text{ex}}$  of  $S+R$ , cross terms between  $S$  and  $R$  vanish, because when  $\mathbf{r}$  is in  $S$  and  $\mathbf{r}'$  in  $R$  (or vice versa) the Coulomb interaction  $|\mathbf{r}-\mathbf{r}'|^{-1}$  vanishes. Thus the exact exchange energy of  $S+R$  becomes a sum of two terms (for  $S$  alone and  $R$  alone), each of which has the form of Eqs. (1) and (3)–(5) with possible fractional occupation at the Fermi level.

Fractional occupation can also be thought of in the language of ensembles. If the wave function of  $S+R$  were fully correlated, the ensemble describing  $S$  would also be fully correlated [17], but since the former is only a single Slater determinant the latter consists of Slater determinants and their probabilities that need not be energy minimized. Now we can use the ensemble describing  $S$  to explain why the Hartree-Fock energy as a function of  $N$  is concave down. Let  $E_i^{\text{HF}}(S;S+R)$  be the Hartree-Fock energy of the  $N_i$ -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  $\sum_i p_i N_i=N$ . Then  $E^{\text{HF}}(S;S+R)=\sum_i p_i E_i^{\text{HF}}(S;S+R) \geq \sum_i p_i E_i^{\text{HF}}(S;S)$ . A familiar and instructive example [20] is the H atom in a spin-restricted stretched  $\text{H}_2$  molecule, where the states  $i$  are the neutral atoms of each spin ( $p_i=0.25$ ,  $N_i=1$ ), cation ( $p_i=0.25$ ,  $N_i=0$ ), and anion ( $p_i=0.25$ ,  $N_i=2$ ). 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 semilocal functionals predict too-negative energies for systems with fractional occupations also becomes clear. By the orthonormality of the orbitals, Eqs. (4) and (5) imply (for any closed or fully separated open system) the sum rule

$$\int d\mathbf{r}' n_x(\mathbf{r},\mathbf{r}') = - \sum_{\sigma} \sum_{\alpha} \frac{f_{\alpha\sigma} n_{\alpha\sigma}(\mathbf{r})}{n(\mathbf{r})}, \quad (6)$$

where  $n_{\alpha\sigma}(\mathbf{r})=f_{\alpha\sigma}|\psi_{\alpha\sigma}(\mathbf{r})|^2$ . Equation (6) for noninteger  $f_{\alpha\sigma}$  was presented without proof in Ref. [13]. Adding and subtracting  $-1=-\sum_{\alpha\sigma} n_{\alpha\sigma}(\mathbf{r})/n(\mathbf{r})$  to Eq. (6), we find

$$\int d\mathbf{r}' n_x(\mathbf{r},\mathbf{r}') = -1 + \sum_{\alpha\sigma} f_{\alpha\sigma}(1-f_{\alpha\sigma}) \frac{|\psi_{\alpha\sigma}(\mathbf{r})|^2}{n(\mathbf{r})}. \quad (7)$$

The close similarity between the integral of  $n_x(\mathbf{r},\mathbf{r}')$  in Eq. (7) and the integral of Eq. (3) for integer  $f_{\alpha\sigma}$  was pointed out

by Gunnarsson and Lundqvist [22], and this similarity persists for noninteger values of  $f_{\alpha\sigma}$ . 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) falls 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 semilocal exchange approximation  $\epsilon_x^{\text{sl}}$  will tend to be more negative than the exact exchange energy per electron  $\epsilon_x^{\text{ex}}(\mathbf{r})$ , as shown in Figs. 1 and 2.

A sum rule for the exact xc-hole density  $n_{xc}(\mathbf{r},\mathbf{r}')$  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 integrand 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 concave-down Hartree-Fock energy of Fig. 1 into the straight-line correlated exact energy. Note also from Fig. 1 that semilocal approximations for  $E_{xc}$  overestimate the strength of exact-degeneracy correlation (which they introduce via  $E_x^{\text{sl}}$ ).

Semilocal functionals are often combined with a Hubbard  $U$  parameter (DFT+ $U$ ). A simple case occurs when only one localized orbital has noninteger occupation  $f$ , and the method adds to the semilocal energy a positive term  $Uf(1-f)$ . Here  $f(1-f)$  is the Hartree-Fock mean square fluctuation of electron number in this orbital. The close connection between DFT+ $U$  and self-interaction correction has been argued [24]. 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 of exact exchange is needed to correct semilocal exchange-correlation approximations. Such a mixing of the concave-down exact exchange with the concave-up semilocal exchange and semilocal correlation can produce the needed straight line. This motivates a local hybrid (lh) functional

$$\epsilon_{xc}^{\text{lh}}(\mathbf{r}) = \epsilon_x^{\text{ex}} + [1-a(\mathbf{r})](\epsilon_x^{\text{sl}} - \epsilon_x^{\text{ex}}) + \epsilon_c^{\text{sl}}, \quad (8)$$

where  $0 \leq a(\mathbf{r}) \leq 1$  and sl=TPSS. Equation (8) was presented in Ref. [25] without a form for  $a(\mathbf{r})$ . Forms were proposed in Ref. [3] and in Ref. [7] (where the term “local hybrid” was coined), but did not achieve useful accuracy for equilibrium properties [7]. The choice  $a(\mathbf{r})=1$  satisfies nearly all universal constraints but misses the delicate and helpful error cancellation between semilocal exchange and semilocal correla-

tion that typically occurs (because the xc-hole is deeper and more short-ranged than the x-hole) in normal regions, i.e., regions of space where the density is not too high, too strongly varying, too one-electron-like, or too fluctuating in a spin-polarized region at the Hartree-Fock level (i.e.,  $\epsilon_x^{\text{ex}}/\epsilon_x^{\text{sl}} \ll 1$ ). So we will take  $a(\mathbf{r})$  to be small or 0 in a normal region, and to tend toward 1 to the extent that any condition of normality is violated. Then the second and third terms on the right-hand side of Eq. (8) represent [19] near-degeneracy static and dynamic correlation, respectively. The dominance of exact exchange [ $a(\mathbf{r}) \rightarrow 1$ ] in the high-density limit means that Eq. (8) has 100% exact exchange plus fully nonlocal correlation.

A natural generalization of the global hybrid of Eq. (2), Eq. (8) can satisfy [3,26] many more exact constraints while achieving greater accuracy. We have developed and are testing [26] 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  $a(\mathbf{r})=1$ . As usual, symmetry must be allowed to break. Spin-symmetry breaking [27], like real correlation, lowers the energy by suppressing Hartree-Fock-level fluctuation of electron number. Semilocal functionals mimic this suppression. Where real correlation cannot fully

suppress fluctuation, as in open systems of noninteger average electron number, semilocal functionals overcorrelate and need a large positive correction, i.e., a large  $a(\mathbf{r})$ .

The Perdew-Zunger self-interaction correction [13] to semilocal 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 semilocal exchange and semilocal correlation in normal regions, and so is inaccurate for molecules near equilibrium geometries [28].

In summary, striking and diverse failures of semilocal 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  $\epsilon_x^{\text{ex}}/\epsilon_x^{\text{sl}} \ll 1$ ) at the Hartree-Fock level. These errors should be corrected by *local* mixing of an  $\mathbf{r}$ -dependent fraction of exact exchange.

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