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Escaping the symmetry dilemma through a pair-density interpretation of spin-density functional theory

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In the standard interpretation of spin-density functional theory, a self-consistent Kohn-Sham calculation within the local spin density (LSD) or generalized gradient approximation (GGA) leads to a prediction of the total energy E, total electron density $n(\mathbf{r})=n_\uparrow(\mathbf{r})+n_\downarrow(\mathbf{r})$, and spin magnetization density $m(\mathbf{r})=n_\uparrow(\mathbf{r})-n_\downarrow(\mathbf{r})$. This interpretation encounters a serious "symmetry dilemma" for H_2, Cr_2, and many other molecules. Without changing LSD or GGA calculational methods and results, we escape this dilemma through an alternative interpretation in which the third physical prediction is not $m(\mathbf{r})$ but the on-top electron pair density $P(\mathbf{r},\mathbf{r})$, a quantity more directly related to the total energy in the absence of an external magnetic field. This alternative interpretation is also relevant to antiferromagnetic solids. We argue that the nonlocal exchange-correlation energy functional, which must be approximated, is most nearly local in the alternative spin-density functional theory presented here, less so in the standard theory, and far less so in total-density functional theory. Thus, in LSD or GGA, predictions of spin magnetization densities and moments are not so robust as predictions of total density and energy. The alternative theory helps to explain the surprising accuracy of LSD and GGA energies, and suggests that the correct solution of the Kohn-Sham equations in LSD or GGA is the fully self-consistent broken-symmetry single determinant of lowest total energy.

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I. INTRODUCTION AND SUMMARY OF CONCLUSIONS

Kohn-Sham spin-density functional theory [1–5] is the most widely used many-electron theory of atoms, molecules, solids, and surfaces. Long applied in condensed-matter physics with the help of the local spin-density (LSD) approximation [1,2], it has recently been adopted in quantum chemistry with the appearance of the more accurate generalized gradient approximation [6–10] (GGA).

For a given external potential $v(\mathbf{r})$ and electron number N, a self-consistent solution of the Kohn-Sham one-electron equations yields a pair of electron spin densities $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$, and a total energy E. If the exact exchange-correlation energy functional (as defined by Kohn and Sham [1–5]) were used in the calculation, these quantities would be the exact physical ground-state spin densities and energy. In practice, the exchange-correlation energy is approximated in LSD or GGA, so that the calculated quantities are not exact. Because LSD and GGA are approximations to this formally exact theory, it is usually believed that the calculated $n_\uparrow(\mathbf{r}),n_\downarrow(\mathbf{r})$, and E are best interpreted as approximations to the corresponding physical quantities, i.e., that $n_\uparrow(\mathbf{r})+n_\downarrow(\mathbf{r})$ predicts the total density $n(\mathbf{r})$, and that $n_\uparrow(\mathbf{r})-n_\downarrow(\mathbf{r})$ predicts the spin magnetization density $m(\mathbf{r})$.

This standard interpretation encounters a serious symmetry dilemma [11,13,14] exemplified by the binding-energy curve of the molecule H_2, which is known to have a singlet ground state [15] with $n_\uparrow(\mathbf{r})=n_\downarrow(\mathbf{r})=n(\mathbf{r})/2$ [16] for all internuclear separations d. In an exact ground-state description of stretched H_2 ($d\rightarrow\infty$), there are two spin-unpolarized hydrogen atoms. At any instant, each has one electron, with negligible number fluctuation and thus vanishing probability for two electrons to come together, as in the familiar spin-polarized hydrogen atom. Suppression of number fluctuations is achieved by the singlet Heitler-London wave function, which is free of the "ionic" configurations ($H^+\cdots H^-$) found in the Hartree-Fock determinant of unbroken singlet symmetry.

At the equilibrium bond length of H_2, the LSD or GGA equations have a single self-consistent ground-state solution with $n_\uparrow=n_\downarrow=n/2$. But, at a larger internuclear separation, this solution bifurcates and a second solution of "broken symmetry" and lower energy appears. In the limit of infinite separation, this second solution describes one hydrogen atom with an electron of spin up on the left, and another with an electron of spin down on the right. The molecular dissociation energies calculated for these two solutions pose a dilemma: The LSD [11,17] or GGA [17] energy is nearly exact for the broken-symmetry solution with qualitatively incorrect spin densities, and seriously in error [11,18] if the correct physical spin symmetry (singlet) is imposed on the spin densities, as shown in Table I. (This symmetry breaking also occurs in Hartree-Fock theory.)

The spin-symmetry dilemma is present for other molecules that dissociate to open-shell atoms. In some cases (e.g., [19,20] Cr_2), the broken-symmetry solution is

TABLE I. Atomization energy of H_2 in electron volts, calculated within spin-unpolarized and spin-polarized versions of the local spin density (LSD) and generalized gradient approximation (GGA) of Ref. [9]. The self-consistent spin-polarized calculations are from Ref. [17]; the spin-unpolarized results were obtained with the help of the atomic spin-polarization energies calculated in Ref. [18]. The zero-point energy (0.26 eV) has been included in the theoretical values.

Spin-unpolarized		Spin-polarized		Expt.
LSD	GGA	LSD	GGA	
6.61	6.88	4.65	4.52	4.49

present and has the lower energy even at the equilibrium bond length. This dilemma has occasioned concern and doubt about spin-density functional theory. Without changing our calculations, we can escape this dilemma through a revolution in our viewpoint. If the approximations cannot be altered the better to fit the formal theory, then the formal theory must be altered the better to fit the approximations.

We begin by noting that although LSD and GGA start from an exact theory, this fact alone does not justify these approximations, which are formally valid only in the limit where $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ vary slowly over space. The success of LSD or GGA in real systems with large density gradients, a tribute to the physical insight of Kohn and Sham, is explained by arguments [3–11] based upon the coupling-constant integral [12] for the approximated exchange-correlation energy, Eq. (A6) of Appendix A. But, within the standard interpretation of spin-density functional theory, these arguments have a weak link: While Eq. (A6) depends directly (although not completely) upon the local density $n(\mathbf{r})$, it has no such direct dependence upon the local spin magnetization density $m(\mathbf{r})$.

In this work, we construct a nearly exact alternative theory, to which LSD and GGA are also approximations, that yields an alternative and preferable physical interpretation in the absence of a strong external magnetic field. In this theory, $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ are *not* the physical spin densities, but are only intermediate objects (like the Kohn-Sham orbitals or Fermi surface [21]), used to construct two physical predictions: the total electron density $n(\mathbf{r})$ from

$$\tilde{n}(\mathbf{r})=n_\uparrow(\mathbf{r})+n_\downarrow(\mathbf{r}) \ , \tag{1}$$

and the on-top electron pair density $P(\mathbf{r},\mathbf{r})$ from its LSD or GGA approximation

$$\tilde{P}(\mathbf{r},\mathbf{r})=P^{\text{unif}}(n_\uparrow(\mathbf{r}),n_\downarrow(\mathbf{r});u=0) \ , \tag{2}$$

where $P^{\text{unif}}(n_\uparrow,n_\downarrow;u=0)$ is the on-top pair density for an electron gas with uniform spin densities $n_\downarrow$ and $n_\downarrow$. (Our comments about the formal properties of GGA apply only to the nonempirical functional constructed [7,9,10] by real-space cutoff of the spurious long-range part of the second-order gradient expansion for the exchange-correlation hole.)

While $n(\mathbf{r})d^3r$ is the probability that an electron will be found in volume element d^3r at $\mathbf{r}$, $P(\mathbf{r},\mathbf{r}')\, d^3r\, d^3r'$ is the probability that an electron will be found in d^3r at $\mathbf{r}$, and another in d^3r' at

$$\mathbf{r}'=\mathbf{r}+\mathbf{u} \ .$$

Thus neither $n(\mathbf{r})$ nor $P(\mathbf{r},\mathbf{r}')$ may be negative, and

$$\int d^3r n(\mathbf{r})=N \ , \tag{3}$$

$$\int d^3r' P(\mathbf{r},\mathbf{r}')=n(\mathbf{r})[N-1] \ . \tag{4}$$

Since (for fixed $n_\uparrow+n_\downarrow$) $P^{\text{unif}}(n_\uparrow,n_\downarrow;u=0)$ is an *even* function of $n_\uparrow-n_\uparrow$, this alternative interpretation encounters no LSD or GGA spin-symmetry dilemma. In the separated-atom limit for H_2, it correctly makes $P(\mathbf{r},\mathbf{r})=0$ for $\mathbf{r}$ in the vicinity of either atom, since (by the Pauli exclusion principle) $P^{\text{unif}}(n_\uparrow,n_\downarrow;u=0)$ vanishes when either $n_\uparrow$ or $n_\downarrow$ vanishes. More generally, we know from numerical studies [22–25] of the uniform electron gas that

$$P^{\text{unif}}(n_\uparrow,n_\downarrow;u=0)\le P^{\text{unif}}(\tilde{n}/2,\tilde{n}/2;u=0) \ . \tag{5}$$

Thus any LSD or GGA calculation can be interpreted in either of two ways: in the usual way, or as an approximation to the alternative nearly exact theory described in this paper. In both interpretations, calculations predict the ground-state energy E and electron density $n(\mathbf{r})$. In the standard interpretation, the spin magnetization density $m(\mathbf{r})=n_\uparrow(\mathbf{r})-n_\downarrow(\mathbf{r})$ is also predicted; in the alternative interpretation presented here, the on-top pair density $P(\mathbf{r},\mathbf{r})$ is predicted instead, via Eq. (2). Even in the alternative interpretation, $n_\uparrow(\mathbf{r})-n_\downarrow(\mathbf{r})$ is the spin magnetization density of the Kohn-Sham noninteracting system, which in many cases may be close to that of the real interacting system, in the same way that the Kohn-Sham Fermi surface [21] is close to the measured one for many crystalline metals.

These two interpretations are equivalent in an electron gas of uniform or slowly varying [26] $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$, where LSD and GGA are strictly valid. If the Kohn-Sham noninteracting wave function is a single Slater determinant, as it normally is in self-consistent LSD or GGA, then the two interpretations are also equivalent in the high-density or noninteracting limits, where single-determinant exchange dominates over correlation and [27]

$$P(\mathbf{r},\mathbf{r})\rightarrow 2n_\uparrow(\mathbf{r})n_\downarrow(\mathbf{r}) \ . \tag{6}$$

[By the "high-density limit", we mean the uniform scaling $n_\sigma(\mathbf{r})\rightarrow\gamma^3 n_\sigma(\gamma\mathbf{r}),\gamma\rightarrow\infty$.] The standard interpretation implies the new one in a fully spin-polarized or low-density electronic system, where $P(\mathbf{r},\mathbf{r})\rightarrow 0$, both exactly and in LSD or GGA.

The alternative interpretation may often be preferable, because of the close relationship between $P(\mathbf{r},\mathbf{r})$ and the electron-electron potential energy

$$\frac{1}{2}\int d^3r \int d^3r' P(\mathbf{r},\mathbf{r}')/|\mathbf{r}'-\mathbf{r}| \ . \tag{7}$$

Thus, accurate total energies are expected to accompany accurate on-top pair densities, as discussed at greater length in Appendix A. Indeed, the new interpretation helps to explain why LSD and GGA yield accurate total energies, and why in practice spin-density functional calculations of the energy are more accurate than total-density ones even in the absence of an external magnetic field, where *formally* $n(\mathbf{r})$ by itself suffices [1–5]. Of course, when there is a strong external magnetic field coupled to the physical spin magnetization density $m(\mathbf{r})$, the alternative interpretation [which makes no prediction for $m(\mathbf{r})$] is inappropriate.

The alternative interpretation seems preferable, not only for molecules like Cr_2 and stretched H_2, but also for many antiferromagnetic solids (where the common eigenstates of $\hat{H}$ and $\hat{S}^2$ have $S=0$). In all these cases, the physical (time-averaged) $m(\mathbf{r})$ vanishes [16], and the rapid variation of $n_\uparrow(\mathbf{r})-n_\downarrow(\mathbf{r})$ from one atom to the next, as found in a LSD or GGA calculation, accounts for the correct $P(\mathbf{r},\mathbf{r})$ arising from strong correlations between electron spins. Only by "freezing" these correlations into $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ can their effect upon $P(\mathbf{r},\mathbf{r})$ be properly described within LSD or GGA.

The importance of the on-top pair density $P(\mathbf{r},\mathbf{r})$ has been stressed by Colle and Salvetti [28], Moscardó and San-Fabián [29], and Becke, Savin, and Stoll [30]. For example, in Ref. [30] the inputs $n(\mathbf{r})$ and $m(\mathbf{r})$ to the LSD or GGA exchange-correlation energy were replaced by $n(\mathbf{r})$ and $P_{\lambda=0}(\mathbf{r},\mathbf{r})$, the noninteracting Kohn-Sham on-top pair density. While Refs. [28–30] proposed alternative methods of calculation employing $P(\mathbf{r},\mathbf{r})$ from a few-determinant wave function, we retain both the existing LSD or GGA functionals and the calculations already performed with them, changing only the physical interpretation of the results.

Aside from its role in Eq. (7), $P(\mathbf{r},\mathbf{r})$ is physically less interesting than $m(\mathbf{r})$. There is, however, a hyperfine term of the relativistic Hamiltonian [31] whose expectation value is proportional to $\int d^3r P(\mathbf{r},\mathbf{r})$.

Before presenting the alternative spin-density functional theory in Sec. III, we pause to discuss the relationship between the pair density and the exchange-correlation hole in Sec. II, and to show numerically that the interpretation of Eqs. (1) and (2) is plausible. Sections IV and V present some concluding remarks, as well as other comments on broken symmetry.

II. ON-TOP EXCHANGE-CORRELATION HOLE: A NUMERICAL STUDY

For any N-electron wave function Ψ, we define [16] the electron pair density

$$\begin{aligned}P(\mathbf{r},\mathbf{r}')&=N(N-1)\sum_{\sigma_1\cdots\sigma_N}\int d^3r_3\cdots d^3r_N|\Psi(\mathbf{r},\sigma_1,\mathbf{r}',\sigma_2,\mathbf{r}_3,\sigma_3,\ldots)|^2\\&=n(\mathbf{r})\left[n(\mathbf{r}')+n_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')\right] .\end{aligned} \tag{8}$$

Here $n_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$ is the density at $\mathbf{r}'$ of the physical ($\lambda=1$, not coupling-constant averaged) exchange-correlation hole surrounding an electron at $\mathbf{r}$. Thus $[n(\mathbf{r}')+n_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')]d^3r'$ is the conditional probability to find an electron in d^3r' at $\mathbf{r}'$, given that there is one at $\mathbf{r}$, and n_{xc} satisfies

$$-n(\mathbf{r}')\le n_{\mathrm{xc}}(\mathbf{r},\mathbf{r}') , \tag{9}$$

$$\int d^3r' n_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')=-1 . \tag{10}$$

If Ψ is a single Slater determinant with spin densities $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$, the exchange-correlation hole reduces to the exchange hole with the properties

$$n_x(\mathbf{r},\mathbf{r}')\le 0 , \tag{11}$$

$$n_x(\mathbf{r},\mathbf{r})=-[n_\uparrow^2(\mathbf{r})+n_\downarrow^2(\mathbf{r})]/n(\mathbf{r}) . \tag{12}$$

For a uniform electron gas, Eq. (8) becomes

$$P^{\mathrm{unif}}(n_\uparrow,n_\downarrow;u)=n[n+n_{\mathrm{xc}}^{\mathrm{unif}}(n_\uparrow,n_\downarrow;u)] . \tag{13}$$

The reader with little feeling for the dependence of $n_{\mathrm{xc}}^{\mathrm{unif}}(u)=n[g^{\mathrm{unif}}(u)-1]$ upon u, n, m, and the coupling-constant λ of Appendix A should consult Fig. 1 and Figs. 3–8 of Ref. [22]. The on-top hole density in the uniform gas, $n_{\mathrm{xc}}^{\mathrm{unif}}(n_\uparrow,n_\downarrow;u=0)$, is known [22,32], not exactly but to good accuracy; see Eqs. (29) and (30) and Table I of Ref. [22].

As shown in Appendix A, the exchange-correlation energy really depends only upon $\langle n_{\mathrm{xc}}(u)\rangle$, the hole averaged over the density of the system, over the direction of $\mathbf{u}$, and over a coupling constant λ. Figure 1 displays $\langle n_{\mathrm{xc}}(u)\rangle$ for the hydrogen atom, evaluated exactly $[n_{\mathrm{xc}}(\mathbf{r},\mathbf{r}+\mathbf{u})=-n(\mathbf{r}+\mathbf{u})]$ and in the LSD approximation $\langle n_{\mathrm{xc}}^{\mathrm{unif}}(u)\rangle$. The LSD description of the averaged on-top hole $\langle n_{\mathrm{xc}}(u=0)\rangle$, and thus of $\langle n_{\mathrm{xc}}(u)\rangle$ for all u, is realistic *only* when the hydrogen atom is treated as a fully spin-polarized system. This remains true even in situations (e.g., stretched H_2) where the atom is really spin unpolarized.

As a numerical test of the alternative interpretation of Eqs. (1) and (2), we must compare the exact on-top exchange-correlation hole density $n_{\mathrm{xc}}(\mathbf{r},\mathbf{r})$ with its LSD or GGA approximation

$$n_{\mathrm{xc}}^{\mathrm{LSD}}(\mathbf{r},\mathbf{r})=n_{\mathrm{xc}}^{\mathrm{unif}}(n_\uparrow(\mathbf{r}),n_\downarrow(\mathbf{r});u=0) . \tag{14}$$

One of the few many-electron systems in which $n_{\mathrm{xc}}(\mathbf{r},\mathbf{r})$ is known exactly is the Hooke's atom [33–35], two electrons bound to a harmonic-oscillator external potential with spring constant k. In Figs. 2 and 3, we make this comparison at the first two values of k for which exact analytic ground-state wave functions are known; the range of densities n for these solutions is typical of valence electrons. We find satisfactory agreement between $n_{\mathrm{xc}}(\mathbf{r},\mathbf{r})$ and $n_{\mathrm{xc}}^{\mathrm{LSD}}(\mathbf{r},\mathbf{r})$, indicating that the inter-

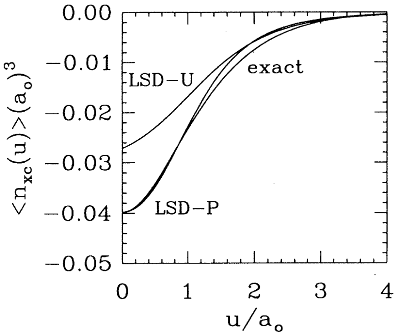

FIG. 1. The exchange-correlation hole for the hydrogen atom as a function of distance $u=|\mathbf{r}'-\mathbf{r}|$ from the electron. The hole has been averaged as in Eq. (A9) over the system [i.e., over $n(\mathbf{r})$], over the direction of $\mathbf{u}$, and over the coupling constant, λ. The exact density has been used to compare the exact hole against two versions of the LSD approximation: U (spin-unpolarized) and P (polarized). Note that "LSD-P" is more negative than "exact" for $u<0.9a_0$, and less negative for $u>0.9a_0$. The exchange-correlation energy (in hartree) is -0.2541 (LSD-U), -0.2902 (LSD-P), -0.3135 (GGA of Ref. [9]), and -0.3125 (exact).

pretation of Eqs. (1) and (2) is plausible.

For the helium atom and the negative hydrogen ion, accurate but nonexact variational wave functions are known [36,37]. Tables II and III show that, once again, the alternative interpretation of Eqs. (1) and (2) is plausible. [Equation (2) is least accurate near the nucleus, where $\nabla^2 n$ diverges.] This conclusion is also consistent with results for the on-top hole density in the H_2 molecule [38] at equilibrium, and in crystalline silicon [39].

The standard and alternative interpretations of spin-density functional theory would be strictly equivalent if the "short-wave-length hypothesis" were true. Some time ago, Langreth and Perdew [40] suggested this hypothesis [41], which amounts [42] to the assertion that LSD is exact for $n_{xc}(\mathbf{r},\mathbf{r})$, or more precisely that the *physical* spin densities at position $\mathbf{r}$ determine $n_{xc}(\mathbf{r},\mathbf{r})$. This assertion is clearly correct at the exchange-only level of Eq. (12) for a single determinant that yields the physical spin densities, and Harris [43] has argued that this fact helps to explain the accuracy of the LSD approximation for the exchange energy. (Refs. [40] and [43] deal only with the spin-unpolarized case $n_\uparrow=n_\downarrow=n/2$, but the

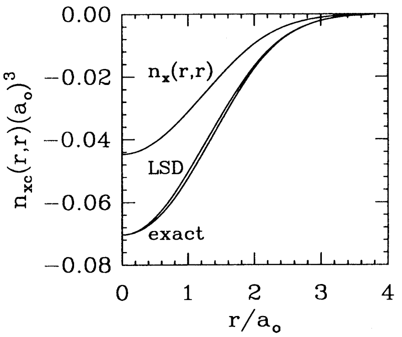

FIG. 2. On-top ($u=0$) exchange [$\lambda=0$, $n_x(\mathbf{r},\mathbf{r})=-n(\mathbf{r})/2$] and exchange-correlation hole ($\lambda=1$) density as a function of electron position r throughout the Hooke's atom with $\hbar\omega=e^2/(2a_0)$, in which $r_s(\mathbf{r})\geq 1.39a_0$, where $r_s(\mathbf{r})=[4\pi n(\mathbf{r})/3]^{-1/3}$. LSD [Eq. (14)] input is from the uniform-gas expression of Ref. [32], as confirmed in Ref. [22]. The exact wave function (Ref. [34]) and density have been used. The exchange-correlation energy (in hartree) is -0.5272 (LSD), -0.5459 (GGA of Ref. [9]), and -0.5536 (exact), from Ref. [35].

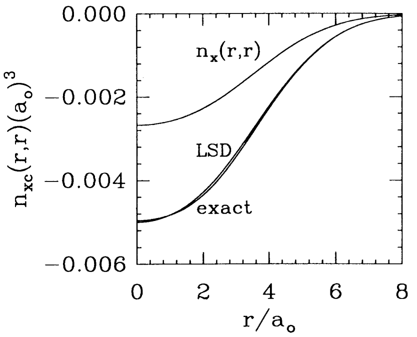

FIG. 3. On-top ($u=0$) exchange [$\lambda=0$, $n_x(\mathbf{r},\mathbf{r})=-n(\mathbf{r})/2$] and exchange-correlation hole ($\lambda=1$) density as a function of electron position r throughout the Hooke's atom with $\hbar\omega=e^2/(10a_0)$, in which $r_s(\mathbf{r})\geq 3.54a_0$, where $r_s(\mathbf{r})=[4\pi n(\mathbf{r})/3]^{-1/3}$. LSD [Eq. (14)] input is from the uniform-gas expression of Ref. [32], as confirmed in Ref. [22]. The exact wave function (Ref. [34]) and density have been used.

TABLE II. On-top ($u=0$) exchange-correlation ($\lambda=1$) hole density $n_{xc}(\mathbf{r},\mathbf{r})$ for an electron at distance r from the nucleus, from the accurate Baker-Hill-Morgan wave function (Ref. [36]), compared with LSD values (Ref. [32]) using the Baker-Hill-Morgan density. Closely similar values for the helium $n_{xc}(\mathbf{r},\mathbf{r})$ have been found by Slamet and Sahni (Ref. [37]) from the Kinoshita wave function. Note that $n_x(\mathbf{r},\mathbf{r})/n(\mathbf{r})=-0.500$. The radial probability density $4\pi r^2 n(r)$ maximizes at $r/a_0=0.57$ for He, and 1.18 for H^-. The numbers of electrons enclosed within this maximum are 0.6 for He and 0.5 for H$^-$.

Atom	r/a_0	$r_s(r)/a_0$	$\frac{n_{xc}(\mathbf{r},\mathbf{r})}{n(\mathbf{r})}$	$\frac{n_{xc}^{\mathrm{LSD}}(\mathbf{r},\mathbf{r})}{n(\mathbf{r})}$
He	0.0	0.404	−0.715	−0.615
	0.2	0.525	−0.709	−0.644
	0.4	0.674	−0.712	−0.675
	0.6	0.856	−0.727	−0.710
	0.8	1.076	−0.753	−0.746
	1.0	1.343	−0.784	−0.783
	1.5	2.275	−0.864	−0.871
	2.0	3.767	−0.923	−0.940
	3.0	9.966	−0.978	−0.996
H$^-$	0.0	0.899	−0.907	−0.717
	0.4	1.169	−0.900	−0.759
	1.0	1.685	−0.889	−0.821
	1.5	2.229	−0.890	−0.859
	2.0	2.870	−0.904	−0.906
	2.5	3.603	−0.925	−0.935
	3.0	4.422	−0.948	−0.956

TABLE III. System-averaged on-top ($u=0$) hole density $N^{-1}\int d^3r\, n(\mathbf{r})n_{\mathrm{xc}}(\mathbf{r},\mathbf{r})$ divided by Z^3 for two-electron ions of nuclear charge Z (in electrons/bohr^3), from the Baker-Hill-Morgan wave function (Ref. [36]). The small LSD errors arise mainly from the region of $\mathbf{r}$ near the nucleus. The high-density ($Z\to\infty$) limit is also shown. X: exchange only ($\lambda=0$, exact and LSD), XC: exchange and correlation at full coupling constant $\lambda=1$.

Z	X	XC (exact)	XC (LSD)
1	-0.0132	-0.0237	-0.0214
2	-0.0239	-0.0345	-0.0325
3	-0.0285	-0.0373	-0.0358
4	-0.0311	-0.0384	-0.0371
∞	-0.0398	-0.0398	-0.0398

general spin-polarized exchange-only case was discussed by Ziegler, Rauk, and Baerends [27].) The numerical results in Figs. 2 and 3 and Tables II and III do not really disprove this hypothesis, since the *exact* $n_{\mathrm{xc}}(\mathbf{r},\mathbf{r})$ is not known, either for the uniform electron gas [22–25,32] or for the two-electron ions [36,37]. Recently, Burke, Perdew, and Langreth [42] disproved the short-wave-length hypothesis by comparing the *exact* high-density limits of the on-top correlation hole density for the Hooke's atom ($k\to\infty$) and for the uniform electron gas ($n\to\infty$). We observe here that a more dramatic failure of this hypothesis occurs in the molecule H_2 at infinite internuclear separation: For $\mathbf{r}$ near either atom, $n_{\mathrm{xc}}(\mathbf{r},\mathbf{r})=-n(\mathbf{r})$ but $n_{\mathrm{xc}}^{\mathrm{unif}}(n(\mathbf{r})/2,n(\mathbf{r})/2;u=0)>-n(\mathbf{r})$. The absolute and relative differences between the two sides of this inequality are greatest where the density $n(\mathbf{r})$ is highest [since $n_{\mathrm{xc}}^{\mathrm{unif}}(n/2,n/2;u=0)\to n_x^{\mathrm{unif}}(n/2,n/2;u=0)=-n/2$ as $n\to\infty$ while $n_{\mathrm{xc}}^{\mathrm{unif}}(n/2,n/2;u=0)\to -n$ as $n\to 0$].

III. ALTERNATIVE SPIN-DENSITY FUNCTIONAL THEORY

Following the general prescription of Jansen [44], it is possible to set up a formal density-functional theory that yields the *exact* energy E, density $n(\mathbf{r})$, and on-top pair density $P(\mathbf{r},\mathbf{r})$. However, since $P(\mathbf{r},\mathbf{r})$ is the expectation value of a *two*-body operator, this theory admits no noninteracting Kohn-Sham system. Instead, we shall set up a formal variational theory with the same structure and the same LSD and GGA approximations as the standard spin-density functional theory, but with the alternative physical interpretation of Eqs. (1) and (2). This variational theory yields an energy that is greater than or equal to the exact ground-state energy, and will typically be very close to it.

We consider a system with Hamiltonian

$$\hat{H}=\hat{T}+\hat{V}_{\mathrm{ee}}+\hat{V}_{\mathrm{ext}}\ , \tag{15}$$

where

$$\hat{T}=\sum_{i=1}^{N}-\frac{1}{2}\nabla_i^2\ , \tag{16}$$

$$\hat{V}_{ee}=\frac{1}{2}\sum_{i}\sum_{j\neq i}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\ , \tag{17}$$

$$\hat{V}_{\mathrm{ext}}=\sum_{i=1}^{N}v(\mathbf{r}_i)\ . \tag{18}$$

Now consider a class of trial functions $n_\uparrow(\mathbf{r}),n_\downarrow(\mathbf{r})$ which have certain properties expected of spin densities: (1) $n_\sigma(\mathbf{r})\geq 0$, (2) $\int d^3r|\nabla n_\sigma^{1/2}(\mathbf{r})|^2<\infty$, (3) $N_\sigma=\int d^3r n_\sigma(\mathbf{r})=\text{integer}$, and (4) $N_\uparrow+N_\downarrow=N$. The "spin densities" found by conventional Kohn-Sham calculations in LSD or GGA have all these properties. Conditions (1)–(4) ensure that there are Slater determinants of finite kinetic energy which yield these spin densities.

With the exception of $n_\uparrow$ and $n_\downarrow$, quantities in this alternative theory are distinguished by a tilda from the corresponding quantities in the standard theory. Following the general idea of Levy's constrained search [45], we define the functional

$$\tilde{F}[n_\uparrow,n_\downarrow]=\min_{\substack{\Psi\to\tilde{n}=n_\uparrow+n_\downarrow,\\ \tilde{P}=P^{\mathrm{unif}}(n_\uparrow,n_\downarrow;u=0)}}\langle\Psi|\hat{T}+\hat{V}_{\mathrm{ee}}|\Psi\rangle\ . \tag{19}$$

This means that, given trial functions $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ from the class defined in the preceding paragraph, we form $\tilde{n}(\mathbf{r})$ and $\tilde{P}(\mathbf{r},\mathbf{r})$ from Eqs. (1) and (2), then search over all normalized and antisymmetric N-electron wave functions Ψ yielding density $\tilde{n}(\mathbf{r})$ and on-top pair density $\tilde{P}(\mathbf{r},\mathbf{r})$ until we find the minimum expectation value. Now define

$$\tilde{E}=\min_{n_\uparrow,n_\downarrow}\left\{\tilde{F}[n_\uparrow,n_\downarrow]+\int d^3r\, v(\mathbf{r})[n_\uparrow(\mathbf{r})+n_\downarrow(\mathbf{r})]\right\}\ , \tag{20}$$

where the minimum is taken over all trial functions $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ subject to the constraints

$$\int d^3r n_\sigma(\mathbf{r})=N_\sigma\ . \tag{21}$$

Clearly, from the Rayleigh-Ritz variational principle,

$$\tilde{E}\geq E\ , \tag{22}$$

where $E=\min_\Psi\langle\Psi|\hat{H}|\Psi\rangle$ is the electronic part of the ground-state energy.

For a given external potential $v(\mathbf{r})$ and electron number N, the energy $\tilde{E}$, the minimizing density $\tilde{n}(\mathbf{r})$ and the on-top pair density $\tilde{P}(\mathbf{r},\mathbf{r})$ are expected to be nearly exact, in view of the many limits (discussed in Sec. I) in which they *are* exact, the numerical results of Sec. II, and the power of variational methods. Moreover, while the Coulomb interaction $1/u$ diverges as $u\to 0$, the effect on the energy of the $u\to 0$ wave-function restriction is reduced by the geometric factor $4\pi u^2$. From Eqs. (2), (5), (8), and (13), a necessary (but not sufficient) condition for the exactness of this alternative theory is the inequality

$$n_{\mathrm{xc}}(\mathbf{r},\mathbf{r})\leq n_{\mathrm{xc}}^{\mathrm{unif}}(n(\mathbf{r})/2,n(\mathbf{r})/2;u=0)\ , \tag{23}$$

which seems to be violated (but very weakly) in Figs. 2 and 3 and Table II. When inequality (23) holds for all $\mathbf{r}$, Eqs. (5) and (13) permit us to find non-negative functions $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ which make the left-hand sides of Eqs. (1) and (2) exact, but there is no reason to expect that those functions each separately integrate to an integer. (As shown in Ref. [30], the inequality (23) is clearly violated in the high-density limit if the Kohn-Sham noninteracting wave function is that sum of two Slater determinants representing the singlet state of two electrons in orthonormal orbitals.)

To derive Kohn-Sham self-consistent equations, we define the noninteracting kinetic energy by

$$T_s[n_\uparrow,n_\downarrow]=\min_{\Phi\to n_\uparrow,n_\downarrow}\langle\Phi|\hat{T}|\Phi\rangle\ , \tag{24}$$

where the search is over all Slater determinants Φ yielding the spin densities $n_\uparrow(\mathbf{r})$, and $n_\downarrow(\mathbf{r})$, and we define the exchange-correlation energy $\tilde{E}_{\rm xc}$ by the equation

$$\tilde{F}[n_\uparrow,n_\downarrow]=T_s[n_\uparrow,n_\downarrow]+U[\tilde{n}]+\tilde{E}_{\rm xc}[n_\uparrow,n_\downarrow]\ , \tag{25}$$

where

$$U[\tilde{n}]=\frac{1}{2}\int d^3r\int d^3r'\,\frac{\tilde{n}(\mathbf{r})\tilde{n}(\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|}\ . \tag{26}$$

At fixed $\tilde{n}(\mathbf{r})$, an increase in $|n_\uparrow(\mathbf{r})-n_\downarrow(\mathbf{r})|$ tends to make $\tilde{E}_{\rm xc}$ (Appendix A) more negative and T_s more positive. Now the Euler equations for the minimization of Eq. (20) are

$$\frac{\delta T_s}{\delta n_\sigma(\mathbf{r})}+\tilde{v}^{\sigma}_{\rm eff}([n_\uparrow,n_\downarrow];\mathbf{r})=\tilde{\mu}_\sigma\ , \tag{27}$$

where the chemical potential $\tilde{\mu}_\sigma$ is the Lagrange multiplier for the constraint (21), and

$$\tilde{v}^{\sigma}_{\rm eff}([n_\uparrow,n_\downarrow];\mathbf{r})=v(\mathbf{r})+\int d^3r'\,\frac{\tilde{n}(\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|}+\frac{\delta\tilde{E}_{\rm xc}}{\delta n_\sigma(\mathbf{r})} \tag{28}$$

is a spin-dependent effective potential. Equation (27) is also the Euler equation for a system of noninteracting electrons with spin densities $n_\uparrow(\mathbf{r}),n_\downarrow(\mathbf{r})$ moving in the external potential $\tilde{v}^{\sigma}_{\rm eff}([n_\uparrow,n_\downarrow];\mathbf{r})$, so we can find $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ from the self-consistent solution of the equations

$$\{-\tfrac{1}{2}\nabla^2+\tilde{v}^{\sigma}_{\rm eff}([n_\uparrow,n_\downarrow];\mathbf{r})\}\tilde{\psi}_{\alpha\sigma}(\mathbf{r})=\tilde{\epsilon}_{\alpha\sigma}\tilde{\psi}_{\alpha\sigma}(\mathbf{r})\ , \tag{29}$$

$$n_\sigma(\mathbf{r})=\sum_{\sigma}|\tilde{\psi}_{\alpha\sigma}(\mathbf{r})|^2\theta(\tilde{\mu}_\sigma-\epsilon_{\alpha\sigma})\ . \tag{30}$$

With the integer $N=N_\uparrow+N_\downarrow$ fixed, $N_\uparrow$ is varied over the integers to minimize $\tilde{E}$.

When $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ vary slowly over space, the local spin-density approximation [1,2]

$$\tilde{E}^{\rm LSD}_{\rm xc}[n_\uparrow,n_\downarrow]=\int d^3r\,n(\mathbf{r})\epsilon_{\rm xc}(n_\uparrow(\mathbf{r}),n_\downarrow(\mathbf{r})) \tag{31}$$

or the generalized gradient approximation [6–11]

$$\tilde{E}^{\rm GGA}_{\rm xc}[n_\uparrow,n_\downarrow]=\int d^3r f(n_\uparrow,n_\downarrow,\nabla n_\uparrow,\nabla n_\downarrow) \tag{32}$$

are valid. In Eq. (31), $\epsilon_{\rm xc}(n_\uparrow,n_\downarrow)$ is the exchange-correlation energy per particle for an electron gas of uniform spin densities $n_\uparrow$ and $n_\downarrow$.

Standard arguments [6–11] for the accuracy of LSD and GGA in real systems are based upon the coupling-constant integral [12] for $E_{\rm xc}$, whose analog in the alternative theory, Eq. (A6), is derived in Appendix A. From this expression, it is clear that the nonlocal exchange-correlation energy functional which must be approximated is most nearly local in this alternative spin-density functional theory, less so in the standard theory, and far less so in total-density functional theory. (Appendix B discusses two different routes from a spin-density to a total-density functional.)

By restricting the search in Eq. (24), we ensure that the Kohn-Sham noninteracting wave function is always a single Slater determinant of the occupied orbitals $\tilde{\psi}_{\alpha\sigma}(\mathbf{r})$. This in turn ensures [27] via Eqs. (6) or (12) that LSD or GGA will yield the correct $P(\mathbf{r},\mathbf{r})$ at the $\lambda=0$ or exchange-only level of the theory. Of course, if the Kohn-Sham potential $\tilde{v}^{\sigma}_{\rm eff}(\mathbf{r})$ has a symmetry, it may have several degenerate Slater determinants as noninteracting ground states, and linear combinations of these will also be noninteracting ground states. As discussed in Sec. V, this situation is not expected to arise for self-consistent Kohn-Sham solutions, at least in LSD or GGA. [However, it is not guaranteed that the self-consistent Kohn-Sham occupation numbers will always obey the ground-state Fermi statistics of Eq. (30).] As discussed further in Appendix A, it appears that in LSD or GGA we should always seek the fully self-consistent single determinant of lowest total energy, no matter what symmetries it may break. (However, an extension [30] of LSD or GGA, applied to a multideterminant Kohn-Sham wave function, has given promising results for multiplet splittings.)

It must never be forgotten that the Kohn-Sham noninteracting and exchange-only ($\lambda=0$) levels of spin-density functional theory are convenient mathematical fictions. Thus, the standard and alternative formal theories can differ at this level, even when both are exact. Stretched H_2 ($d\to\infty$) provides an example, which is discussed further in Appendix A.

IV. CONCLUDING REMARKS ON THE ALTERNATIVE THEORY

Unlike the standard spin-density functional theory, the alternative theory presented in Sec. III does not always yield the exact ground-state total energy and electron density. Nevertheless, this alternative theory is exact at its single-determinant exchange-only level, exact for the uniform electron gas, and exact in the fully spin-polarized and low-density limits, and would probably be much more accurate than its LSD or GGA approximations in applications to real electronic systems. For the reasons discussed near the end of Sec. I and in Appendix A, LSD and GGA are likely to be better approximations to this alternative theory than to the standard one, in the absence of a strong external magnetic field. Moreover, the physical interpretation of this alternative theory does not lead to a symmetry dilemma within LSD or GGA, because the alternative theory makes no prediction for $m(\mathbf{r})$.

Although fictitious spin-dependent scalar potentials have been invoked in the noninteracting inhomogeneous and interacting uniform (or slowly varying) reference systems, no physical magnetic fields are allowed in the alternative theory. The standard theory, which attempts to represent the effects of such fields, is somewhat inconsistent in its neglect of electron currents [46] which also couple to those fields.

The practical message emerging from this investigation is clear: In the absence of an external magnetic field, LSD and GGA calculations always predict the total energy E, electron density $n(\mathbf{r})$, and on-top pair density $P(\mathbf{r},\mathbf{r})$ for a many-electron ground state, via Eqs. (1) and (2). They also predict the spin magnetization density $m(\mathbf{r})$ via $n_\uparrow(\mathbf{r})-n_\downarrow(\mathbf{r})$, but the reliability of this prediction is more questionable than that of $P(\mathbf{r},\mathbf{r})$. The predicted $m(\mathbf{r})$ is quite incorrect for molecules (when the internuclear separation is large enough), and for certain antiferromagnetic solids [47]. Solid chromium, for example, has a spin-density wave ground-state often modeled as an antiferromagnetic lattice [48]. Based on the alternative interpretation presented here, it is clear that LSD or GGA should *not* be expected to make a reliable prediction of the spin moment of each atom for these systems.

The spiral spin-density wave in solid Cr also illustrates that the orientation of $\mathbf{m}(\mathbf{r})$ need not be confined to a single fixed axis. When it is not, the standard spin-density functional theory becomes more complicated, with $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ replaced by a nondiagonal spin-density matrix [2] $n_{\sigma\sigma'}(\mathbf{r})$. However, since $P(\mathbf{r},\mathbf{r})$ has no vector character, no complication arises in the alternative theory.

Neither the standard nor the alternative ground-state spin-density functional is required to predict excitation energies in general, or multiplet splittings in particular. The standard functional (i.e., the exact $E[n_\uparrow,n_\downarrow]$ as defined by Kohn and Sham [1–5]) should, however, yield the same total energy for the spin densities of different degenerate ground states; in the standard interpretation, LSD should (but notoriously does not [49]) yield the same energy for the $M_s=0$ as for the $M_s=\pm1$ triplet states of the carbon atom with $S=1$. This is *not* expected of the alternative functional [as defined in Eqs. (19) and (20)], where $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ are meaningful only when and insofar as they produce an absolute minimum of the energy.

In the standard interpretation, the minimizing $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ may be used to determine the total spin S_{tot} of the ground state; LSD and GGA sometimes make the wrong prediction. For example [10], for the molecule C_2 at equilibrium, the predicted S_{tot} equals one although the true S_{tot} equals zero. The LSD or GGA energy of the triplet is a little lower even than that of the broken-symmetry singlet (in which the spin moments are concentrated not on the individual atoms but on opposite sides of the bond axis [10]). In the alternative interpretation, where no spin determination may be made, no such problem arises.

Besides C_2, there may be many other systems in which the standard interpretation of LSD or GGA leads to an incorrect prediction of the total spin S_{tot}. For example, O_2 really has $S_{\text{tot}}=1$ at equilibrium, and also presumably in the limit of large internuclear separation. But a LSD or GGA calculation in this limit will force each O atom into a state with $S=1$ and $M_s=\pm1$, leading to $M_{s,\text{tot}}=\pm2$ and $S_{\text{tot}}=2$, or to $M_{s,\text{tot}}=0$ and $S_{\text{tot}}=0$.

V. OTHER COMMENTS ON BROKEN SYMMETRY

Although we have escaped from the most disturbing symmetry dilemmas of spin-density functional theory, a few other symmetry issues remain to be discussed.

(1) Within the standard spin-density functional theory or the alternative of Sec. III, there is no obvious reason why the Kohn-Sham effective potential $v^\sigma_{\text{eff}}(\mathbf{r})$ should always have the same symmetry as the external potential $v(\mathbf{r})$, or why the Kohn-Sham noninteracting wave function should always have the same symmetry as the true ground-state wave function. In fact, since $n(\mathbf{r})$ and its components $n_\uparrow(\mathbf{r}),n_\downarrow(\mathbf{r})$ may have a lower symmetry than $v(\mathbf{r})$, so may the effective potential constructed from $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ [14]. For example, the Kohn-Sham LSD Slater determinant need not be an eigenfunction of the square of the total spin $\hat{S}^2$ and in many open-shell atomic and molecular systems it is not [50,51] (although it often comes closer [38] than does the unrestricted Hartree-Fock wave function). Pople, Gill, and Handy [52] have discussed the benefits of allowing this "spin contamination" of Kohn-Sham calculations.

(2) Methods [27–30,53] have been developed to deal with the case where the Kohn-Sham noninteracting wave function is a linear combination of degenerate Slater determinants, so that Eqs. (6) and (12) are lost. But degeneracy is usually a consequence of symmetry, and the allowable symmetry-breaking described under point (1) should ensure that the self-consistent LSD or GGA Kohn-Sham noninteracting wave function is a single determinant. For example, the self-consistent LSD or GGA effective potential for an open-shell atom may be nonspherical [54].

(3) Symmetry-breaking may be avoided in certain formal density functional theories. An example is the theory of Görling [14], in which the symmetries of the external potential and true ground-state wave function are propagated to the Kohn-Sham effective potential and noninteracting wave function, at the high price of a symmetry dependence of the needed density functional. Another example is the zero-temperature limit of Mermin's theory [55], in which ensembles replace wave functions and the ground-state density has the symmetry of the external potential. In the absence of an external magnetic field, the Görling and Mermin theories are examples of total- (not spin-) density functional theories.

In LSD, the energy of an atom is nearly the same whether the atomic density is spherically averaged or not, but GGA is somewhat more sensitive [56] to the angular shape of the density, as Table IV shows. Within the standard interpretation, both LSD and GGA *are* sensitive to the spin-magnetization density $\mathbf{m}(\mathbf{r})$; averaging this quantity over all directions in space leads [44] to a total-density functional theory in which LSD and GGA are considerably less accurate, as is evident from Table I.

(4) The exact ground-state total density $n(\mathbf{r})$ itself may have certain symmetries (dictated by those of the wave

TABLE IV. Atomization energy of O_2 in electron volts, calculated from spherically averaged and nonspherical atomic densities within LSD and within the GGA of Refs. [7] and [8]. The nonspherical atomic density is constructed from cubic-harmonic orbitals (s,p_x,p_y,p_z) which belong to a spherically averaged Kohn-Sham potential; relaxing this shape constraint would reduce the total energy of the separated atoms, and thus might further improve the GGA atomization energy (from Ref. [56]).

Spherical atoms		Nonspherical atoms		Expt.
LSD	GGA	LSD	GGA	
7.5	6.6	7.5	5.9	5.2

function) [57] which LSD or GGA fail to reproduce. In view of the results of Table IV, this sort of symmetry breaking may not have much effect on the total energy. Of greater concern is the absence of a derivative discontinuity [58] of E_{xc} in continuum approximations such as LSD or GGA, leading to improper dissociation of heteronuclear molecules to fractionally charged fragments [58,59]. Despite these concerns, the evidence for the usefulness of Kohn-Sham LSD and especially GGA calculations in solid-state physics [10,60–62] and quantum chemistry [10,63–66] is now overwhelming.

Note added in proof. There is another physical application for the integral of the on-top pair density over all space, besides the one given at the end of Sec. I. This integral also determines the large-wave-vector limit of system-averaged electron-electron structure factor, as shown by Kimball [72].

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APPENDIX A: COUPLING-CONSTANT INTEGRATION FOR $\tilde{E}_{xc}$

Here we shall derive an analog of the standard coupling-constant integration [12] for $\tilde{E}_{xc}$ defined by Eq. (25). To do so, we consider the Hamiltonian

$$\hat{H}_\lambda = \hat{T} + \lambda \hat{V}_{ee} + \sum_\sigma \int d^3r \hat{n}_\sigma(\mathbf{r}) v_\lambda^\sigma(\mathbf{r}) \ , \tag{A1}$$

in which the electron-electron interaction involves a coupling constant λ, and the spin-dependent external potentials $v_\lambda^\sigma(\mathbf{r})$ are adjusted to hold $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ fixed for all λ, according to the generalizations of Eqs. (1) and (2),

$$\tilde{n}(\mathbf{r}) = n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r}) \tag{A2}$$

is the λ-independent total density, and

$$\tilde{P}_\lambda(\mathbf{r},\mathbf{r}) = P_\lambda^{\text{unif}}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}); u=0) \tag{A3}$$

is the on-top pair density for coupling constant λ. When $\lambda=1$, we have the real system of interest. When $\lambda=0$, we have the Kohn-Sham noninteracting system with on-top pair density given by Eq. (6).

For each λ, we define

$$\begin{aligned}\tilde{E}_\lambda &= \min_{\substack{\Psi \to \tilde{n} = n_\uparrow + n_\downarrow, \\ \tilde{P} = P_\lambda^{\text{unif}}(n_\uparrow, n_\downarrow; u=0)}} \langle \Psi | \hat{H}_\lambda | \Psi \rangle \ , \\ &= \langle \tilde{\Psi}_\lambda | \hat{H}_\lambda | \tilde{\Psi}_\lambda \rangle \ .\end{aligned} \tag{A4}$$

From the variational principle, we expect that $\partial \tilde{E}_\lambda / \partial \lambda = \langle \tilde{\Psi}_\lambda | \partial \hat{H}_\lambda / \partial \lambda | \tilde{\Psi}_\lambda \rangle$, with an error that is very small because our alternative formal theory is nearly exact for the energy. Thus

$$\begin{aligned}\tilde{E}_1 - \tilde{E}_0 = &\int_0^1 d\lambda \langle \tilde{\Psi}_\lambda | \hat{V}_{ee} | \tilde{\Psi}_\lambda \rangle \\ &+ \sum_\sigma \int d^3r n_\sigma(\mathbf{r}) [v(\mathbf{r}) - \tilde{v}_{\text{eff}}^\sigma([n_\uparrow, n_\downarrow]; \mathbf{r})] \ ,\end{aligned} \tag{A5}$$

or

$$\tilde{E}_{xc} = \int_0^1 d\lambda \frac{1}{2} \int d^3r \int d^3r' \frac{\tilde{n}(\mathbf{r}) \tilde{n}_{xc}^\lambda(\mathbf{r},\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} \ , \tag{A6}$$

where $\tilde{n}_{xc}^\lambda(\mathbf{r},\mathbf{r}')$ is the variationally determined exchange-correlation hole for coupling strength λ, which reduces to $\tilde{n}_{xc}(\mathbf{r},\mathbf{r}')$ at $\lambda=1$ and to $\tilde{n}_x(\mathbf{r},\mathbf{r}')$, the exact exchange hole of the alternative theory, at $\lambda=0$.

The LSD approximation of Eq. (31) can also be written in the form of Eq. (A6),

$$\begin{aligned}\tilde{E}_{xc}^{\text{LSD}} = &\int_0^1 d\lambda \frac{1}{2} \int d^3r \int d^3r' \\ &\times \frac{\tilde{n}(\mathbf{r}) n_{xc}^{\text{unif},\lambda}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}); |\mathbf{r}' - \mathbf{r}|)}{|\mathbf{r}' - \mathbf{r}|} \ ,\end{aligned} \tag{A7}$$

where $n_{xc}^{\text{unif},\lambda}(n_\uparrow, n_\downarrow; u)$ is the hole density for coupling strength λ at interelectronic separation u in a uniform electron gas. The exact, LSD, and GGA exchange-correlation energies all have the real-space analysis

$$\tilde{E}_{xc} = \frac{N}{2} \int_0^\infty du \, 4\pi u^2 \langle \tilde{n}_{xc}(u) \rangle / u \ , \tag{A8}$$

where $\langle \tilde{n}_{xc}(u) \rangle$ is the appropriate hole averaged over the system, over the coupling constant, and over the direction of $\mathbf{u} = \mathbf{r}' - \mathbf{r}$:

$$\langle \tilde{n}_{xc}(u) \rangle = \int \frac{d\hat{u}}{4\pi} \int_0^1 d\lambda \frac{1}{N} \int d^3r \, \tilde{n}(\mathbf{r}) \tilde{n}_{xc}^\lambda(\mathbf{r}, \mathbf{r} + \mathbf{u}) \ . \tag{A9}$$

The variationally determined exchange-correlation hole for coupling strength λ, $\bar{n}^{\lambda}_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$, has all of the general properties described in Sec. II. Most of these [Eqs. (10)–(12) and Eq. (9) for $\mathbf{r}'=\mathbf{r}$] are respected by the LSD and GGA approximations to this hole, and the resulting constraints on the integrals for the energy help to justify LSD and GGA for real electronic systems. Moreover, the LSD and GGA holes satisfy [42] the exact cusp condition for $\mathbf{r}'\approx\mathbf{r}$ at each λ.

By adopting as our solution to the Kohn-Sham equations (29) and (30) the fully self-consistent broken-symmetry single determinant of lowest total energy, we ensure that the LSD or GGA on-top exchange hole $\bar{n}^{\lambda=0}_{\mathrm{xc}}(\mathbf{r},\mathbf{r})=\bar{n}_x(\mathbf{r},\mathbf{r})$ is appropriate [via Eq. (12)] for the $\lambda=0$ or exchange-only level. The need for a single-determinant Kohn-Sham wave function in LSD was stressed by Ziegler, Rauk, and Baerends [27] within the standard interpretation of spin-density functional theory.

Note that the exchange-correlation hole $\bar{n}_{\mathrm{xc}}(\mathbf{r},\mathbf{r}+\mathbf{u})$ is deeper and more short-ranged (in u) than the exchange hole $\bar{n}_x(\mathbf{r},\mathbf{r}+\mathbf{u})$. As a result, the nonlocalities of exchange and correlation tend to cancel [10], and this fact also works in favor of LSD and GGA.

Finally, we discuss the problem of stretched H_2 from the viewpoint of Eq. (A6). Let the bond length d tend to infinity before any other limits are taken. Then $P(\mathbf{r},\mathbf{r})=0$ for all $\mathbf{r}$, and the alternative formal theory of Sec. III is exact. In the alternative formal theory, the variationally determined wave function $\tilde{\Psi}_\lambda$ will tend continuously as $\lambda\rightarrow 0$ to a single Slater determinant of broken singlet symmetry. But, in the standard formal theory [1–5], Ψ_λ for *all* λ is the Heitler-London wave function [71] for $\lambda=1$, a linear combination of two degenerate pure-singlet Slater determinants, one with two electrons of opposite spin in the bonding orbital and the other with two electrons of opposite spin in the antibonding orbital. [With *any* $\lambda>0$, the interaction λ/r will suppress the ionic configurations ($H^+\cdots H^-$) present in a single Slater determinant of unbroken singlet symmetry.] This failure to connect $\Psi_{\lambda=1}$ adiabatically to a single Slater determinant as $\lambda\rightarrow 0$ is what causes the large error of the spin-unpolarized LSD atomization energy in Table I. [For finite *d*, the Kohn-Sham wave function $\Psi_{\lambda=0}$ *is* a single Slater determinant with two electrons in the bonding orbital. As *d* increases, Ψ_λ resembles $\Psi_{\lambda=1}$ over a wider range of the interval $0<\lambda<1$, so that the contribution to the integral (A6) from the $\lambda=0$ limit becomes negligible as $d\rightarrow\infty$.]

APPENDIX B: TWO ROUTES FROM SPIN-DENSITY TO TOTAL-DENSITY FUNCTIONALS

In the absence of an external magnetic field, the total density $n(\mathbf{r})$ plays the same *formal* role [1–5] as $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$. Here we shall draw the connection between total-density and spin-density functionals in both the standard and alternative theories, following the argument of Jansen [44].

First we define

$$F[n]=\min_{n_\uparrow,n_\downarrow\rightarrow n} F[n_\uparrow,n_\downarrow]$$

$$=T_s[n]+U[n]+E_{\mathrm{xc}}[n]\ , \tag{B1}$$

$$T_s[n]=\min_{n_\uparrow,n_\downarrow\rightarrow n} T_s[n_\uparrow,n_\downarrow]\ , \tag{B2}$$

where the spin-density functionals are minimized in a search over all trial functions $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ which sum to $n(\mathbf{r})$ and have the properties listed at the beginning of Sec. III. Then

$$E=\min_n\left\{F[n]+\int d^3r\, v(\mathbf{r})n(\mathbf{r})\right\}\ . \tag{B3}$$

Equations (B1) and (B2) do *not* imply that

$$E_{\mathrm{xc}}[n]=E_{\mathrm{xc}}[n/2,n/2]\ , \tag{B4}$$

unless the minimizing $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ from Eqs. (B1) and (B2) each happen to equal $n(\mathbf{r})/2$. Thus, if we start with a local (LSD) approximation for $E_{\mathrm{xc}}[n_\uparrow,n_\downarrow]$, Eqs. (B1) and (B2) can provide a highly nonlocal approximation for $E_{\mathrm{xc}}[n]$.

LSD and GGA are derived for slowly varying $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$, where the minimizations in Eqs. (B1) and (B2) are expected to yield $n_\uparrow=n_\downarrow=n/2$. [For a slowly varying but very low n, the minimization in (B1) may lead to $n_\uparrow=n$ and $n_\downarrow=0$, but usually with negligible energetic consequences.] Thus, Eq. (B4) provides the prescription for constructing an LSD or GGA functional for $E_{\mathrm{xc}}[n]$ from one for $E_{\mathrm{xc}}[n_\uparrow,n_\downarrow]$.

We have presented two routes from spin-density to total-density functionals. Within LSD or GGA, the former [Eqs. (B1) and (B2)] is more accurate while the latter [Eq. (B4)] is simpler.

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