PHYSICAL REVIEW A **90**, 032513 (2014)

Approximating the exchange energy through the nonempirical exchange-factor approach

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(Received 20 June 2014; published 29 September 2014)

Various widely used approaches for the exchange-correlation energy of Kohn-Sham theory, such as the generalized gradient approximation and hybrid methods, suffer from the one-electron self-interaction error. This error manifests itself in one-electron or two-electron spin-unpolarized systems. We propose new approximations to the exchange energy that are exact for the mentioned problems. Starting from the weighted density approximation (WDA), we introduce several weighting factors (that we refer to as exchange factors) which are designed to reproduce various properties of the exact exchange hole. Furthermore, a new exact condition for the exchange factor is presented that concerns the asymptotic behavior of the exchange hole as one electron coordinate moves out to infinity. Observance of this and other conditions results in exchange functionals that improve upon the WDA.

DOI: 10.1103/PhysRevA.90.032513 PACS number(s): 31.15.eg

I. INTRODUCTION

In Kohn-Sham (KS) density functional theory [1–5], the difficult-to-account-for components of the ground-state energy are lumped into the exchange-correlation term E_{XC}. Over the years numerous approximations to E_{XC} have been developed, the earliest one being the local density approximation (LDA) proposed by Kohn and Sham [1]. Another more sophisticated type of representation of E_{XC} is the generalized gradient approximation (GGA) [3–8]. It gives useful results for properties such as geometries, vibrational frequencies, and binding energies [3] that can be further improved if hybrids, i.e., GGAs with fractional inclusion of exact exchange, are employed [9–12]. These local or semilocal functionals, or approximations based on them, are plagued by the self-interaction error. The self-interaction error leads to undesired consequences in the calculation of response properties, excitations energies, electron distributions, etc. More recent methods of increased complexity that also suffer from the self-interaction error, albeit to a lesser extent, are meta-GGAs (e.g., [13,14]) and double-hybrids (for a recent review see [15]).

A promising avenue to address the self-interaction problem is to turn to completely nonlocal density functionals and to use exact exchange augmented by a suitable correlation functional. This is a route that is presently pursued by various groups [16,17] including our own [18,19]. Another successful cure [20] for the self-interaction problem is the range separation of the Coulomb repulsion combined with the construction of separate hybrids for the resulting short- and long-range contributions.

In the present work, we also address the one-electron self-interaction problem. We focus on the exchange energy of electrons, which is given by

$$E_X = \int d^3r\rho(\mathbf{r})\epsilon(\mathbf{r}) = \int d^3r d^3u \, \frac{\rho(\mathbf{r})\rho_X(\mathbf{r},\mathbf{u})}{2u}, \tag{1}$$

where $\mathbf{r}$ is the position of the reference electron and $\mathbf{u} = \mathbf{r}' - \mathbf{r}$ is the electron-electron separation, with $\mathbf{r}'$ as the coordinate of the second electron. $\rho_X(\mathbf{r},\mathbf{u})$ is the exchange hole as, for instance, discussed in detail in [21]. For later reference, the exchange energy per particle

$$\epsilon(\mathbf{r}) = \int d^3u \, \frac{\rho_X(\mathbf{r},\mathbf{u})}{2u} \tag{2}$$

is introduced. Even though in the present work we focus on exchange, the self-interaction error in an approximation to the correlation functional can be eliminated using ideas very similar to the ones described here for exchange. We return to this point in the conclusions. To approximate E_X, we employ completely nonlocal schemes that extend on the weighted density approximation (WDA) [22–27]. In the WDA, the electron density at any position in space contributes to $\epsilon(\mathbf{r})$ at the reference point $\mathbf{r}$. This approximation starts from an explicit ansatz for the exchange hole,

$$\rho_X(\mathbf{r},\mathbf{u}) = f_X(\mathbf{r},u)\rho(\mathbf{r}+\mathbf{u}). \tag{3}$$

Deviating somewhat from the established notation in the WDA, we use the exchange factor $f_X(\mathbf{r},u)$ in this expression. Usually in the WDA this factor is closely related to the pair correlation function g of the homogeneous electron gas with one subtracted out (i.e., $g - 1$). Since we considerably modify this choice, we introduce the notion exchange factor. To emphasize the difference between Eq. (3) and local and semilocal approximations to the exchange hole, we note that in local and semilocal approximations the right-hand side would depend not on $\rho(\mathbf{r}+\mathbf{u})$, but on $\rho(\mathbf{r})$ and $(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}))$, respectively. An important property of the WDA is that for a properly designed $f_X(\mathbf{r},u)$, one-electron problems and closed-shell two-electron problems are dealt with exactly, thus the corresponding self-interaction error is eliminated at this level.

In very recent work on the WDA [28,29] it has been shown that the imposition of suitable conditions, such as symmetry with respect to the exchange of $\mathbf{r}$ and $\mathbf{r}'$ in $\rho(\mathbf{r})\rho_X(\mathbf{r},\mathbf{r}' - \mathbf{r})$, can improve upon the original WDA. The complexity of implementing this condition is considerable, however.

In the present work we design various versions of $f_X(\mathbf{r},u)$, ensuring that all of them are exact for one-electron systems

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and two-electron spin-unpolarized systems, while also trying to approach the performance of GGAs for truly multielectron problems. To move towards this goal, we impose varying conditions on the approximate exchange hole that have been identified previously as being important. In more detail, we use an exchange hole model for the homogeneous electron gas that was developed in [30] and [31] as a starting point for the construction of $f_X(\mathbf{r},u)$ in Eq. (3). We design $f_X(\mathbf{r},u)$ such that several constraints are satisfied that have not been considered in the original WDA or subsequent modifications thereof. In particular, we consider the curvature of the exchange hole at its origin ($u=0$) [32] and ensure that our model reproduces its exact value. Furthermore, we also demonstrate that the exchange factor does not vary in regions of zero density and we enforce this condition in the design of $f_X(\mathbf{r},u)$.

The formal developments that are presented in Sec. II are implemented in the Gaussian program system [33] as described in Sec. III and put to the test through calculations of total exchange energies and exchange-energy contributions to atomization energies of molecules (Sec. IV).

II. THE EXCHANGE-FACTOR MODEL

The considerations in this section are based on the assumption that the system is spin unpolarized. For spin-polarized systems, the conventional spin-scaling relations (see, e.g., [21]) are employed to convert the formulas derived here to their spin-polarized counterparts. As described in Sec. I, we start from the exchange-factor ansatz, Eq. (3), for the exchange hole $\rho_X(\mathbf{r},\mathbf{u})$. The choice for $f_X(\mathbf{r},u)$ that is equivalent to the WDA is to equate it to the function $J(y)$ as defined by Ernzerhof and Perdew [30],

$$J(y) = -\frac{A}{y^2}\frac{1}{1+(4/9)Ay^2} + \left(\frac{A}{y^2}+B+Cy^2+Ey^4\right)e^{-Dy^2}, \qquad (4)$$

where $y=k_F u$ and $k_F=(3\pi^2\rho)^{1/3}$. $J(y)$ is a nonoscillatory version of the scaled LDA exchange hole, i.e.,

$$\rho_X^{\mathrm{LDAnosc}}(\mathbf{r},u) = J(k_F u)\rho(\mathbf{r}). \qquad (5)$$

$J(y)$ is designed to reproduce the physically relevant features of the exact LDA exchange hole. The numerical values of the parameters in this model are derived in Ref. [21]. Employing $J(y)$ in the exchange-factor ansatz results in

$$\rho_X(\mathbf{r},\mathbf{u}) = J(k_F u)\rho(\mathbf{r}+\mathbf{u}). \qquad (6)$$

This expression for $\rho_X(\mathbf{r},u)$ does not respect the important normalization condition:

$$\text{Condition I:} \quad \int d^3u\,\rho_X(\mathbf{r},u) = -1. \qquad (7)$$

In the WDA, this problem is remedied by replacing k_F with an effective Fermi vector k_F^{eff} that is determined such that the normalization condition is restored. The most important feature of the WDA is that it cures a serious deficiency of local and semilocal approximations. In the LDA and GGA the exchange hole is centered around the reference point at $\mathbf{r}$. This means that a reference electron which is very far from the density of a finite system will have an exchange hole centered around itself, away from the actual density where it should be. The WDA remedies this shortcoming since, by construction, the exchange hole is a hole in the density of the system, i.e., the hole cannot be deeper than $-1/2\rho(\mathbf{r}+\mathbf{u})$, or equivalently,

$$\text{Condition II:} \quad -\frac{\rho_X(\mathbf{r},\mathbf{u})}{\rho(\mathbf{r}+\mathbf{u})} \geqslant \frac{1}{2}. \qquad (8)$$

This condition, violated by the LDA and GGA, ensures that the WDA becomes exact for one-electron systems and two-electron, closed-shell systems. For instance, in two-electron spin-unpolarized systems the only way to satisfy the normalization condition is to have $f_X(\mathbf{r},u)=-1/2$, which results in the exact expression $\rho_X(\mathbf{r},\mathbf{u})=-\frac{1}{2}\rho(\mathbf{r}+\mathbf{u})$.

To further improve upon the original WDA, we first define the angle average of the electron density $\rho(\mathbf{r}+\mathbf{u})$ over all possible orientations of $\mathbf{u}$:

$$\rho(\mathbf{r},u) = \int \frac{d\Omega_{\mathbf{u}}}{4\pi}\rho(\mathbf{r},\mathbf{r}+\mathbf{u}). \qquad (9)$$

For the evaluation of $\epsilon(\mathbf{r})$, only the spherically averaged exchange hole $\rho_X(\mathbf{r},u)$ [30], defined by

$$\rho_X(\mathbf{r},u) = \int \frac{d\Omega_{\mathbf{u}}}{4\pi}\rho_X(\mathbf{r},\mathbf{r}+\mathbf{u}), \qquad (10)$$

is needed. For simplicity, all the exchange factors that we consider here are independent of the orientation of $\mathbf{u}$; they depend only on $u=|\mathbf{u}|$. Our final exchange-factor ansatz for the spherically averaged exchange hole is, thus,

$$\rho_X(\mathbf{r},u) = f_X(\mathbf{r},u)\rho(\mathbf{r},u), \qquad (11)$$

where the design of $f_X(\mathbf{r},u)$ is, of course, the crucial step. We base our strategy on exact conditions, avoiding fits to experimental data. As in the case of the WDA, we impose normalization (condition I). Another constraint that the WDA satisfies and that we retain is the on-top value condition,

$$\text{Condition III:} \quad \rho_X(\mathbf{r},u=0) = -\tfrac{1}{2}\rho(\mathbf{r}). \qquad (12)$$

Obviously, Eq. (12) is satisfied if $f_X(\mathbf{r},u=0)=-\frac{1}{2}$, which is the case for all versions of $f_X(\mathbf{r},u)$ considered here.

A constraint that we state here for the first time and include subsequently in our approximation is that for finite systems $f_X(\mathbf{r},u)$ is constant in empty space. If we consider the asymptotic behavior of the KS wave function, we find [34]

$$\lim_{|\mathbf{r}_1|\to\infty}\Phi_{\mathrm{KS}} \sim \sqrt{\frac{\rho(\mathbf{r}_1)}{4N}}\alpha(1)\Phi_{\mathrm{KS}}^{N-1} - \sqrt{\frac{\rho(\mathbf{r}_1)}{4N}}\beta(1)\Phi_{\mathrm{KS}}^{N-1}, \qquad (13)$$

where Φ_{KS}^{N-1} is the Slater determinant for $N-1$ electrons, constructed with the KS orbitals of the N-electron system. α and β are the spin functions. With Eq. (13) it is easy to verify that the KS pair density $P_{\mathrm{KS}}(\mathbf{r},\mathbf{r}')$ satisfies

$$\lim_{|\mathbf{r}|\to\infty} P_{\mathrm{KS}}(\mathbf{r},\mathbf{r}') = 1/2\rho(\mathbf{r})\rho^{N-1}(\mathbf{r}'). \qquad (14)$$

Using $P_{\mathrm{KS}}(\mathbf{r},\mathbf{r}')=1/2\rho(\mathbf{r})\rho(\mathbf{r}')+1/2\rho(\mathbf{r})\rho_X(\mathbf{r},\mathbf{r}')$ it follows that

$$\text{Condition IV:} \quad \lim_{|\mathbf{r}|\to\infty} f_X(\mathbf{r},u) = -1/2. \qquad (15)$$

This indicates that $f_X(\mathbf{r},u)$ does not vary but remains constant at $-1/2$ for large values of $|\mathbf{r}|$ in comparison to u. To include this condition, we replace $k_F u$ with a function $\mu(u)$:

$$f_X(\mathbf{r},u) = J(\mu(u)). \tag{16}$$

Suitable versions of $\mu(u)$ are constructed which ensure that we recover the LDA in the homogeneous electron gas limit,

$$\text{Condition V:}\quad 4\pi \int u^2 du \frac{f_X(\mathbf{r},u)\rho(\mathbf{r},u)}{2u} = \epsilon^{\mathrm{LDA}}[\rho] \quad \text{for} \quad \rho(\mathbf{r}) = \rho. \tag{17}$$

Since in the homogeneous limit, the proper variable of $J(y)$ is $y = k_F u = (3\pi^2\rho)^{1/3}u$, a possible replacement of this variable in inhomogeneous systems satisfies $d\mu_1 = k\rho^{1/3}(\mathbf{r},u)du$. Integration leads to

$$\mu_1(u) = k\int_0^u dy \rho^{\frac{1}{3}}(\mathbf{r},y), \tag{18}$$

where k, here as in the other expressions for μ, is determined such that the normalization condition is satisfied. If the electron density $\rho(\mathbf{r},u)$ vanishes, the infinitesimal change of $\mu_1(u)$ upon variation of u is 0, i.e., $d\mu_1 = 0$ for $\rho(\mathbf{r},u) = 0$. This means that $f_X(\mathbf{r},u)$ does not vary in empty space. Another appropriate expression for $\mu(u)$ is

$$\mu_2(u) = k\left(4\pi\int_0^u dy y^2 \rho(\mathbf{r},y)\right)^{\frac{1}{3}}. \tag{19}$$

Apparently, $\mu_2(u)$ is proportional to the number of electrons inside a sphere of radius u around the reference electron. This also implies that a certain value of the electron-electron distance, represented by $\mu_2(u)$, cannot be exceeded in a finite system [the same is true for $\mu_1(u)$]. Other than $\mu_1(u)$ and $\mu_2(u)$, there are infinitely more substitution functions that fulfill the same constraints as $\mu_1(u)$ and $\mu_2(u)$. In Sec. IV, we present an additional one, $\mu_3(u)$, which is designed to improve the numerical results obtained with $\mu_1(u)$ and $\mu_2(u)$.

To further expand the exchange-factor model, conditions that have been identified as important in the past can be taken into account. In the construction of approximate exchange holes often the curvature of the exchange hole at the origin ($u = 0$) is the focus of attention. Either it is ensured that this curvature is accurately approximated (e.g., in the Ernzerhof-Perdew exchange hole of Ref. [30]) or the exact curvature is explicitly imposed as an additional condition [13,32]. In a spin-unpolarized system, the curvature of the exchange hole is given by

$$\text{Condition VI:}\quad \rho_X^{(2)}(\mathbf{r}) = \left.\frac{d^2\rho_X(\mathbf{r},u)}{du^2}\right|_{u=0} = \frac{1}{6}\left(-\nabla^2\rho(\mathbf{r}) + 4\left[\tau(\mathbf{r}) - \frac{|\nabla\rho(\mathbf{r})|^2}{8\rho(\mathbf{r})}\right]\right). \tag{20}$$

Here $\tau(\mathbf{r}) = \frac{1}{2}\sum_i^N \nabla\varphi_i(\mathbf{r})\nabla\varphi_i(\mathbf{r})$ is the positive, semidefinite kinetic energy density. Through variation of the constant C in the ansatz for $J(y)$ in Eq. (4) the exact curvature can be imposed, while at the same time the normalization condition is enforced through variation of the parameter k. This leads to coupled equations that are solved through an iterative procedure. If the value of C required to satisfy the curvature condition deviates too much from the LDA value of C, no solution for k can be obtained. To avoid this problem, a smooth cutoff function is used for the curvature that limits the range of C values. In detail, the exact curvature $\rho_X^{(2)}(\mathbf{r})$ is replaced by its LDA value $\rho_X^{\mathrm{LDA}(2)}(\mathbf{r})$ plus a correction term,

$$\rho_X^{(2)}(\mathbf{r}) \approx \rho_X^{\mathrm{LDA}(2)}(\mathbf{r}) + \gamma(\rho_X^{(2)}(\mathbf{r}) - \rho_X^{\mathrm{LDA}(2)}(\mathbf{r})), \tag{21}$$

where the damping function γ is given by

$$\gamma(x) = \frac{x}{1+\delta|x|}. \tag{22}$$

The value of $\delta = \frac{12.95077}{k_F^2\rho}$ is the lowest value for which solutions for the parameter k can still be found. Clearly for small deviations of the exact curvature from the LDA value, the exact curvature is reproduced by our model hole since in this case $\gamma(x) = x$.

A further condition satisfied by the exact E_X of a finite system is that the corresponding asymptotic exchange potential $v_X(\mathbf{r})$ exhibits a Coulomb behavior,

$$\text{Condition VII:}\quad v_X(\mathbf{r}) = \frac{\delta E_X[\rho]}{\delta\rho(\mathbf{r})} \overset{|r|\to\infty}{\sim} -\frac{1}{r}. \tag{23}$$

As has been pointed out previously (see, e.g., [28]), in the conventional WDA a Coulombic asymptotic behavior is obtained, albeit with the wrong prefactor of $1/2$. To examine the asymptotic behavior of $v_X(\mathbf{r})$ for our approximations, we start from

$$\begin{aligned} v_X(\mathbf{r}') &= \frac{\delta}{\delta\rho(\mathbf{r}')}4\pi\int u^2 du d^3r \frac{\rho(\mathbf{r})f_X(\mathbf{r},u)\rho(\mathbf{r},u)}{2u} \\ &= \frac{\delta}{\delta\rho(\mathbf{r}')}\int d^3u d^3r \frac{\rho(\mathbf{r})f_X(\mathbf{r},u)\rho(\mathbf{r}+\mathbf{u})}{2u} \\ &\overset{r'\to\infty}{\sim} \int d^3u d^3r \frac{\left[\frac{\delta}{\delta\rho(\mathbf{r}')}\rho(\mathbf{r})\right]f_X(\mathbf{r},u)\rho(\mathbf{r}+\mathbf{u})}{2u} \\ &\quad + \int d^3u d^3r \frac{\rho(\mathbf{r})f_X(\mathbf{r},u)\left[\frac{\delta}{\delta\rho(\mathbf{r}')}\rho(\mathbf{r}+\mathbf{u})\right]}{2u}. \end{aligned} \tag{24}$$

The term involving the derivative of $f_X(\mathbf{r},u)$ with respect to the density vanishes for $r' \to \infty$. The first term on the right-hand side of Eq. (24) simplifies to

$$\begin{aligned} &\int d^3u d^3r \frac{\left[\frac{\delta}{\delta\rho(\mathbf{r}')}\rho(\mathbf{r})\right]f_X(\mathbf{r},u)\rho(\mathbf{r}+\mathbf{u})}{2u} \\ &= \int d^3u \frac{\rho(\mathbf{r}'+\mathbf{u})f_X(\mathbf{r}',u)}{2u} \\ &\overset{r'\to\infty}{\sim} \frac{1}{2r'}\int d^3u \rho(\mathbf{r}'+\mathbf{u})f_X(\mathbf{r}',u) \\ &= -\frac{1}{2r'}. \end{aligned} \tag{25}$$

For the second term we find

$$\int d^3r d^3u \frac{\rho(\mathbf{r}) f_X(\mathbf{r},u)\big[\frac{\delta}{\delta\rho(\mathbf{r}')}\rho(\mathbf{r}+\mathbf{u})\big]}{2u}$$
$$= \int d^3r d^3u \frac{\rho(\mathbf{r}) f_X(\mathbf{r},u)\delta(\mathbf{r}'-(\mathbf{r}+\mathbf{u}))}{2u}$$
$$\overset{r'\to\infty}{\sim} \frac{1}{2r'}\int d^3r \rho(\mathbf{r}) f_X(\mathbf{r},r'). \quad (26)$$

While there is no simple answer to the question of what the value of $\lim_{r'\to\infty}\int d^3r\rho(\mathbf{r})f_X(\mathbf{r},r')$ is, this quantity is in general nonzero for a nontrivial choice of $\mu(u)$, such as $\mu_1(u)$ and $\mu_2(u)$. If $\mu(u) = k_F^{\mathrm{eff}}u$, i.e., for the conventional version of the WDA, this term vanishes since in this case $f_X(\mathbf{r},u) = 0$ for $u \to \infty$. In total, we obtain a $v_X(\mathbf{r})$ that behaves as $-\mathrm{const.}/r$ with const. $\in (0.5,1]$. This means that we improve upon the $v_X(\mathbf{r})$ of the conventional WDA, for which $v_X(\mathbf{r}) \overset{r\to\infty}{\sim} -1/(2r)$. This is an indication that the use of a function $\mu(u)$ has a physical significance beyond the enforcement of condition IV. In principle, by variation of the coefficient E in Eq. (4) or by other more radical modifications of $J(y)$, we should be able to design $f_X(\mathbf{r},u)$ such that $\lim_{|\mathbf{r}'|\to\infty}\int d^3r\rho(\mathbf{r})f_X(\mathbf{r},r') = -1$, resulting in the correct asymptotic behavior of v_X.

III. IMPLEMENTATION OF THE EXCHANGE-FACTOR MODEL

To illustrate the proposed approximations, we implement the exchange-factor model in the Gaussian03 [33] program system. All our approximations are purposefully constructed in terms of spherically averaged densities $\rho(\mathbf{r},u)$. As we explain now, in a program based on Gaussian basis functions, the spherical average can be done analytically. This way, the angular variables are eliminated and the integration remaining in the computation of $\epsilon(\mathbf{r})$ is one-dimensional. In terms of basis functions, the electron density of the molecular orbital i at point $\mathbf{r}$ is expressed as

$$\rho_i(\mathbf{r}) = \sum_{\alpha\beta} C_{\alpha i}C_{\beta i}\sum_{pq} D_{p\alpha}D_{q\beta}\chi_p(\mathbf{r})\chi_q(\mathbf{r}). \quad (27)$$

In this equation, $D_{p\alpha}$ denotes a contraction coefficient, while $C_{\alpha i}$ is an expansion coefficient for a molecular orbital. The total density is then obtained by summing over all occupied molecular orbitals. A primitive Gaussian centered at an atom at position $\mathbf{A}$ is given by

$$\chi_p(\mathbf{r}-\mathbf{A}) = N_p(x-A_x)^l(y-A_y)^m(z-A_z)^n e^{-\gamma_p|\mathbf{r}-\mathbf{A}|^2}, \quad (28)$$

where N_p is a normalization constant. The parameters l, m, and n also depend on p. If we define two new quantities,

$$\mathbf{r}_A = \mathbf{r}-\mathbf{A} = (x-A_x)\hat{\mathbf{x}} + (y-A_y)\hat{\mathbf{y}} + (z-A_z)\hat{\mathbf{z}} \quad (29)$$

and

$$\mathbf{S}_A = S_{A_x}\hat{\mathbf{S}}_\mathbf{x} + S_{A_y}\hat{\mathbf{S}}_\mathbf{y} + S_{A_z}\hat{\mathbf{S}}_\mathbf{z}, \quad (30)$$

we can rewrite the primitive Gaussians as

$$\chi_p(\mathbf{r}_A) = N_p\frac{\partial^l}{\partial S_{A_x}^l}\frac{\partial^m}{\partial S_{A_y}^m}\frac{\partial^n}{\partial S_{A_z}^n} e^{-\gamma_p r_A^2+\mathbf{S}_A\cdot\mathbf{r}_\mathbf{A}}\bigg|_{\mathbf{S}_A=0}. \quad (31)$$

The spherically averaged molecular orbital density is given by

$$\rho_i(\mathbf{r},u) = \int\frac{d\Omega_u}{4\pi}\rho_i(\mathbf{r}+\mathbf{u})$$
$$= \sum_{\alpha\beta pq} C_{\alpha i}C_{\beta i}D_{p\alpha}D_{q\beta}\int\frac{d\Omega_u}{4\pi}\chi_p(\mathbf{r}+\mathbf{u}-\mathbf{A})$$
$$\cdot\chi_q(\mathbf{r}+\mathbf{u}-\mathbf{B}), \quad (32)$$

where $\mathbf{B}$ is another index for the atomic centers. Using the expression in Eq. (31) and defining the vector

$$\mathbf{w} = \mathbf{S}_A + \mathbf{S}_B - 2\gamma_p\mathbf{r}_A - 2\gamma_q\mathbf{r}_B, \quad (33)$$

we can formulate the main equation of our implementation of the spherical average,

$$\int\frac{d\Omega_u}{4\pi}\chi_p(\mathbf{r}+\mathbf{u}-\mathbf{A})\cdot\chi_q(\mathbf{r}+\mathbf{u}-\mathbf{B})$$
$$= \left(\frac{\partial^l}{\partial S_{A_x}^l}\frac{\partial^m}{\partial S_{A_y}^m}\frac{\partial^n}{\partial S_{A_z}^n}\frac{\partial^{\bar{l}}}{\partial S_{B_x}^{\bar{l}}}\frac{\partial^{\bar{m}}}{\partial S_{B_y}^{\bar{m}}}\frac{\partial^{\bar{n}}}{\partial S_{B_z}^{\bar{n}}}G(\mathbf{S}_A,\mathbf{S}_B)\right)_{\mathbf{S}_A=\mathbf{S}_B=0}, \quad (34)$$

where

$$G(\mathbf{S}_A,\mathbf{S}_B) = N_pN_q e^{-\gamma_p(r_A^2+u^2)+\mathbf{S}_A\cdot\mathbf{r}_A}\cdot e^{-\gamma_q(r_B^2+u^2)+\mathbf{S}_B\cdot\mathbf{r}_B}$$
$$\cdot\frac{1}{2wu}(e^{wu}-e^{-wu}). \quad (35)$$

With this expression, formulas are generated and implemented for every combination of l, m, n, $\bar{l}$, $\bar{m}$, $\bar{n}$. Once the spherically averaged density is available, the integrations over $|\mathbf{u}|$, required to enforce the normalization condition and to calculate $\epsilon(\mathbf{r})$, are performed numerically. The integrations over d^3r, required to obtain E_X, are done using the already implemented numerical integration schemes of the Gaussian program system [33].

To obtain $\epsilon(\mathbf{r})$ the exchange hole of the factorization ansatz is normalized through variation of the constant k and, if required, the coefficient C in Eq. (4) is adjusted such that the hole reproduces the exact curvature. The latter step then results in the violation of the normalization condition and the next cycle of an iterative procedure is initiated. In this iterative procedure, the value of the normalization constant k is obtained through a combination of Newton-Raphson and bisection algorithms. Even though the computational effort is higher compared to conventional local and semilocal approximations, efficient implementations of the exchange-factor approach can be obtained, since the calculation of $\epsilon(\mathbf{r})$ on the spatial grid points can be parallelized on modern computers containing tens of computational cores.

IV. APPLICATIONS OF THE EXCHANGE-FACTOR MODEL

In this section we present exchange energies of atoms and molecules that are calculated with the Gaussian program system [33]. The geometries of the molecules are determined

TABLE I. Absolute values of exchange energies (in Hartree) of atoms and molecules. Results obtained with the various substitution functions [$\mu_0(u) = ku$ (equivalent to the WDA), $\mu_1(u) = k\int_0^u dy\rho^{\frac{1}{3}}(\mathbf{r},y)$, $\mu_2(u) = k[4\pi\int_0^u dyy^2\rho(\mathbf{r},y)]^{\frac{1}{3}}$, and $\mu_3(u) = k[4\pi\int_0^u dyy^2\rho^{1/2}(\mathbf{r},y)]^{\frac{1}{3}}$] are listed, as well as the corresponding approximations which also satisfy the curvature condition (indicated by C). MAE, mean absolute error. MAEs of certain subsets of systems as well as total MAEs are reported.

Atom	WDA	WDAC	μ_1	μ_1C	μ_2	μ_2C	μ_3	μ_3C	Exact	LSD	PBE
H	0.308	0.308	0.308	0.308	0.308	0.308	0.308	0.308	0.308	0.265	0.303
He	1.017	1.017	1.017	1.017	1.017	1.017	1.017	1.017	1.017	0.878	1.008
Li	1.782	1.789	1.711	1.726	1.640	1.655	1.727	1.740	1.773	1.533	1.752
Be	2.699	2.718	2.509	2.547	2.316	2.355	2.549	2.584	2.664	2.313	2.636
B	3.839	3.863	3.589	3.638	3.313	3.365	3.637	3.682	3.755	3.290	3.724
C	5.216	5.247	4.914	4.971	4.570	4.634	4.966	5.020	5.052	4.473	5.017
N	6.844	6.882	6.491	6.559	6.086	6.162	6.544	6.608	6.574	5.879	6.531
O	8.570	8.613	8.147	8.223	7.621	7.713	8.202	8.275	8.173	7.356	8.142
F	10.547	10.596	10.064	10.147	9.452	9.556	10.115	10.196	9.988	9.054	9.967
Ne	12.787	12.843	12.247	12.333	11.560	11.674	12.290	12.381	12.042	10.991	12.023
Na	14.859	14.920	14.245	14.344	13.445	13.573	14.282	14.381	13.979	12.764	13.928
P	24.142	24.229	23.188	23.318	21.920	22.091	23.180	23.312	22.612	20.783	22.491
Cl	29.387	29.488	28.221	28.378	26.683	26.871	28.182	28.328	27.484	25.341	27.333
MAE	0.506	0.546	0.192	0.219	0.422	0.342	0.182	0.219	0.000	0.808	0.043
BH	4.176	4.205	3.902	3.957	3.586	3.648	3.960	4.010	4.112	3.612	4.081
CH	5.555	5.589	5.228	5.291	4.832	4.905	5.289	5.347	5.394	4.789	5.366
NH	7.186	7.226	6.807	6.878	6.339	6.423	6.869	6.936	6.900	6.189	6.874
OH	8.962	9.007	8.529	8.606	7.975	8.070	8.587	8.662	8.517	7.704	8.510
FH	11.000	11.051	10.512	10.597	9.884	9.989	10.565	10.648	10.367	9.454	10.375
Na_2	29.728	29.849	28.311	28.514	26.011	26.297	28.503	28.702	27.944	25.526	27.856
MAE	0.562	0.615	0.166	0.195	0.768	0.650	0.186	0.228	0.000	0.993	0.031
N_2	13.718	13.789	12.889	13.023	11.880	12.043	13.052	13.176	13.084	11.859	13.118
NO	15.444	15.519	14.540	14.682	13.403	13.579	14.707	14.840	14.668	13.337	14.721
CO	13.920	13.992	13.090	13.226	12.079	12.243	13.250	13.377	13.278	12.033	13.303
F_2	21.099	21.193	19.974	20.141	18.418	18.638	20.143	20.304	19.869	18.171	19.948
P_2	48.297	48.468	46.140	46.405	42.652	43.026	46.270	46.533	45.145	41.598	44.973
Cl_2	58.809	59.009	56.211	56.509	52.007	52.422	56.289	56.583	54.967	50.767	54.708
MAE	1.712	1.826	0.476	0.533	1.762	1.510	0.470	0.633	0.000	2.208	0.104
Total MAE	0.809	0.870	0.254	0.288	0.827	0.696	0.252	0.321	0.000	1.188	0.055

with the PBE [8] exchange-correlation functional using the $6\text{–}311+G(2d,p)$ basis set [33]. The resulting converged density matrices are employed to calculate the exchange energies within the various approximations as well as the exact exchange energy. The exchange-energy contribution to the atomization energy, i.e., $\Delta E_X = E_X^{\text{molecule}} - E_X^{\text{atoms}}$, is also determined. The calculations reported are done spin unrestricted using spin-density functionals.

In addition to the conditions satisfied by the LSD, the WDA ensures that the exchange hole is a hole in the density (condition II). This constraint leads to results for total exchange energies of atoms that are considerably improved compared to the LSD (see Table I). On the order of 37% of the error in the LSD is removed. For ΔE_X of singly bonded molecules (upper part of Table II) a slight worsening is obtained, while for congested molecules a significant improvement is observed. By congested, we mean that several electron pairs are involved in the chemical bond, either as binding or as antibinding pairs. Overall, the WDA improves upon the LSD for ΔE_X as well as for E_X; the performance of the PBE is not reached, however. We should add that for one-electron and two-electron spin-unpolarized systems the WDA is, of course, exact.

The curvature condition, which appears to be important to improve upon local approximations [13,32], is considered next. Somewhat unexpectedly, this condition worsens the mean absolute errors for the total energies compared to the WDA; ΔE_X values are slightly improved, however. The curvature condition is a crucial element in the construction of GGAs, which reproduce the system average of the curvature of the exchange hole to a good approximation [30]. GGAs are not exact for one-electron systems but they dramatically improve the total exchange energies. This can be seen in Table I, where PBE results are listed. Unfortunately, the beneficial impact of the curvature condition does not carry over from GGAs to the realm of the WDA.

Next we investigate the impact of condition IV, which stipulates that the exchange factor does not vary in empty space. We devised several functions $\mu(u)$ that enforce this condition. $\mu_1(u)$ reduces the error in the total exchange energy considerably; this is particularly pronounced for congested molecules. ΔE_X values of singly bonded, hydrogen-containing systems are worse than the WDA, whereas the atomization energies of congested systems are virtually unchanged compared to the WDA. Another substitution function that we consider is $\mu_2(u)$, which satisfies the same constraints as $\mu_1(u)$ but performs worse. This indicates that a considerable spread in the quality of the results is obtained even though the physical conditions satisfied are the same. We consider this ambiguity in

TABLE II. Exchange-energy contributions to the atomization energies (in Hartree) obtained with the various substitution functions [$\mu_0(u) = ku$ (equivalent to the WDA), $\mu_1(u) = k\int_0^u dy\rho^{\frac{1}{3}}(\mathbf{r},y)$, $\mu_2(u) = k[4\pi\int_0^u dyy^2\rho(\mathbf{r},y)]^{\frac{1}{3}}$, and $\mu_3(u) = k[4\pi\int_0^u dyy^2\rho^{1/2}(\mathbf{r},y)]^{\frac{1}{3}}$] are listed, as well as the corresponding approximations which also satisfy the curvature condition (indicated by C). MAE, mean absolute error. MAEs of certain subsets of systems as well as total MAEs are reported.

Molecule	WDA	WDAC	μ_1	μ_1C	μ_2	μ_2C	μ_3	μ_3C	Exact	LSD	PBE
BH	−0.029	−0.034	−0.004	−0.011	0.034	0.026	−0.014	−0.020	−0.049	−0.058	−0.054
CH	−0.031	−0.034	−0.006	−0.011	0.045	0.037	−0.015	−0.019	−0.034	−0.051	−0.046
NH	−0.033	−0.035	−0.007	−0.011	0.055	0.047	−0.016	−0.019	−0.018	−0.045	−0.040
OH	−0.084	−0.086	−0.073	−0.075	−0.046	−0.049	−0.077	−0.078	−0.036	−0.083	−0.065
FH	−0.145	−0.147	−0.140	−0.141	−0.124	−0.125	−0.142	−0.143	−0.071	−0.135	−0.105
Na_2	−0.009	−0.009	0.180	0.174	0.880	0.849	0.060	0.059	0.014	0.002	0.001
MAE	0.031	0.030	0.059	0.056	0.194	0.186	0.035	0.034	0.000	0.030	0.019
N_2	−0.030	−0.024	0.094	0.094	0.293	0.280	0.037	0.041	0.063	−0.100	−0.057
NO	−0.029	−0.024	0.099	0.100	0.304	0.295	0.040	0.044	0.078	−0.102	−0.048
CO	−0.134	−0.132	−0.029	−0.031	0.112	0.104	−0.083	−0.082	−0.054	−0.204	−0.143
F_2	−0.006	−0.001	0.154	0.154	0.486	0.474	0.086	0.088	0.107	−0.063	−0.014
P_2	−0.013	−0.010	0.236	0.231	1.189	1.157	0.090	0.091	0.078	−0.032	0.009
Cl_2	−0.034	−0.034	0.232	0.247	1.358	1.321	0.075	0.074	0.000	−0.084	−0.042
MAE	0.086	0.083	0.085	0.087	0.578	0.559	0.034	0.032	0.000	0.143	0.095
Total MAE	0.059	0.057	0.072	0.071	0.386	0.373	0.035	0.033	0.000	0.086	0.057

an exploratory fashion by considering the substitution function

$$\mu_3(u) = k\left(4\pi\int_0^u dyy^2\rho^{1/2}(\mathbf{r},y)\right)^{\frac{1}{3}}. \tag{36}$$

$\mu_3(u)$ differs from $\mu_2(u)$ [Eq. (19)] through the fact that the square root of the density is taken under the integral sign. The motivation for this adjustment is provided by the observation that the WDA, which corresponds to $\mu(u) = ku$, overestimates the absolute values of the exchange energies, while $\mu_2(u)$ underestimates them. Correspondingly a substitution function that is "more constant" than $\mu_2(u)$ is expected to yield improved results. An example of such a substitution function is obtained by taking the square root of the density under the integral sign [Eq. (36)]. In the homogeneous limit, the electron density is a constant and therefore $\mu_3(u)$ is proportional to $\mu_2(u)$ in this limit. Since the constant k in $\mu_3(u)$ is determined to ensure normalization, two substitution functions that are proportional are in fact identical. Therefore, $\mu_3(u)$ satisfies the same conditions as $\mu_1(u)$ and $\mu_2(u)$, including condition V, i.e., it reproduces the correct exchange-energy density in the homogeneous limit. As can be seen in Tables I and II, very good results are obtained that even improve upon the PBE for ΔE_X. Finally, we discuss the combined impact of condition IV and condition VI. As in the case of the WDA, and opposed to the experience gained in the construction of exchange functionals hitherto, the inclusion of the curvature condition does not result in an overall improvement compared to the functionals building only on the substitution function $\mu(u)$.

The exchange factors considered in the numerical illustrations satisfy an increasing number of exact conditions. Starting from the WDA, where $f_X(\mathbf{r},u)$ is provided by the homogeneous electron gas, additional exact conditions are introduced to improve the approximations. While the results fall behind the expectations in the sense that the performance of the PBE exchange functional for total exchange energies of atoms and molecules is not met, we get close to this performance for ΔE_X then using the substitution function $\mu_1(u)$. With the substitution function $\mu_3(u)$ the ΔE_X values obtained even improve upon the PBE. The curvature condition (condition VI) does not yield conclusive improvements upon introduction into the various exchange-factor models. This is the more surprising since the curvature of the exchange hole is a key ingredient in the construction of various exchange functionals (see, e.g., [13,30,32]). We suspect that the WDA and the subsequent exchange-factor models are unbalanced approximations in the sense explained now. The ansatz, Eq. (11), deviates from local and semilocal exchange holes through the use of the spherically averaged density $\rho(\mathbf{r},u)$. While the use of $\rho_X(\mathbf{r},u)$ results in the exact exchange hole for systems with one electron of a given spin, this cannot be said about the many-electron case, where the exchange factor has a nontrivial form and is no longer known exactly. This combination of exact [$\rho(\mathbf{r},u)$] and approximate [$f(\mathbf{r},u)$] factors in Eq. (11) appears to be more demanding than the simultaneous approximation of both factors. Local and semilocal approximations can be viewed as schemes in which the entire exchange hole is approximated instead of its individual factors.

V. CONCLUSIONS AND OUTLOOK

The development of functionals for the exchange-correlation energy of KS theory is an area that continuously evolves and, by the very nature of approximations, will never result in a functional satisfying all the criteria imposed by practitioners and theoreticians. The former will find cases where the functional fails, while the latter will identify important conditions that are not satisfied by a given approximation. Any approximation is a compromise reflecting its designers' preferences and it has imperfections. In our work, we pursue an approach to the construction of functionals that draws on exact conditions. We provide a list of important properties to be satisfied by approximations to the exchange hole and expand this list through the addition of a new condition derived from the asymptotic behavior of the wave function. By imposing an increasing number of conditions from this list, holes of increasing complexity are obtained, which often result in improved exchange energies compared to the original WDA. The ultimate objective of our work is to obtain an exchange-correlation functional that shows a performance similar to that of established GGAs for multielectron systems, while being exact for one-electron cases; the present work is a step towards this goal. The relative importance of various conditions is discussed and it appears that the curvature condition (condition VI) has a largely insignificant impact in the exchange-factor-based schemes, whereas the condition of no variation of $f_X(\mathbf{r},u)$ in empty space (condition IV) is quite useful. This is an unexpected deviation from the behavior found in the construction of GGAs. This finding should be of importance for the systematic construction of exchange factors and WDA-type functionals. Interestingly, the introduction of the function $\mu(u)$ to satisfy condition IV also improves the asymptotic behavior of the resulting exchange potential. The correct asymptotic behavior of the exchange potential is sometimes thought to be related to the symmetry of $\rho(\mathbf{r})\rho_X(\mathbf{r},\mathbf{r}'-\mathbf{r})$ with respect to the exchange of $\mathbf{r}$ and $\mathbf{r}'$ (this is the consequence of a corresponding symmetry of the pair density). This symmetry is, however, not crucial to obtain the exact asymptotic behavior of $v_X(\mathbf{r})$, as shown by our consideration.

For the inclusion of correlation effects in the exchange-factor model, we envision the development of an appropriate correlation factor $f_C(\mathbf{r},u)$ in an ansatz of the form

$$\begin{aligned}\rho_{XC}(\mathbf{r},u) &= f_C(\mathbf{r},u)\rho_X(\mathbf{r},u)\\ &= f_C(\mathbf{r},u)f_X(\mathbf{r},u)\rho(\mathbf{r},u).\end{aligned} \tag{37}$$

$f_C(\mathbf{r},u)$ is again constructed to satisfy a number of conditions known about the exchange-correlation hole. One of them is the normalization condition. Another obvious condition (analogous to condition II) to impose on the exchange-correlation hole is $-\frac{\rho_{XC}(\mathbf{r},\mathbf{u})}{\rho(\mathbf{r}+\mathbf{u})} \geqslant 1$, which, in combination with the normalization condition, ensures that the resulting exchange-correlation hole is one-electron self-interaction-free. In the past we developed correlation factors to represent the PBE exchange-correlation hole [18] and to turn exchange holes that yield the exact $\epsilon_X(\mathbf{r})$ into exchange-correlation holes [19]. In future work, we will describe the construction of an appropriate correlation factor for the exchange-factor model.

ACKNOWLEDGMENT

We would like to acknowledge the financial support provided by The Natural Sciences and Engineering Research Council of Canada (NSERC).

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