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Fourth-order series expansion of the exchange hole

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Approximate functionals for the exchange-correlation energy of electrons often draw on explicit or implicit models for the exchange-correlation hole. Here we focus on the spherically averaged exchange hole $\rho_{\mathrm{X}}(\mathbf{r},u)$, which depends on the reference point $\mathbf{r}$ and on the electron-electron distance u. We extend the well-known [A. D. Becke and M. R. Roussel, Phys. Rev. A **39**, 3761 (1989)] second-order Taylor-series expansion in u to fourth order and we show that the fourth-order term can add important additional information that is particularly relevant for molecules compared to atoms. Drawing on these findings, we explore exchange functionals that depend on the fourth-order term of the expansion of $\rho_{\mathrm{X}}(\mathbf{r},u)$. We also find that Gaussian basis set expansions, frequently used in electronic structure codes, result in unsatisfactory representations of the fourth-order term.

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I. INTRODUCTION

Kohn-Sham (KS) density-functional theory (DFT) [1–9] has become an invaluable method in many areas such as chemistry and materials physics. Its success is founded in accurate approximations to the exchange-correlation energy E_{XC}. An early approximation to E_{XC} is the local spin density approximation (LSD) [2] which employs the exact exchange-correlation energy per particle (ϵ_{XC}) of the homogeneous electron gas (HEG). More sophisticated approximations are for instance the generalized gradient approximations (GGAs), hybrids, meta-GGAs, hyper-GGAs, etc. (for overviews see for instance [8–10]).

While no strategy is known for a systematic improvement of approximations to E_{XC}, there are various avenues available for further development. One such avenue builds on the exchange-correlation hole [3,4,11]. Particular models for the exchange hole have been analyzed and refined (see, e.g., [11–17]) and they are the starting point for exchange-correlation functionals employing for instance the correlation factor approach [18,19] or range-separation techniques (see, e.g. [17,20,21]).

In the present work, we focus on the spherically averaged exchange hole (see, e.g. [3,11,13]) $\rho_{\mathrm{X}}(\mathbf{r},u)$ that depends on the reference position $\mathbf{r}$ and on the electron-electron distance u. This hole is often represented [22–24] through a Taylor series expansion in powers of u,

$$\rho_{\mathrm{X}}(\mathbf{r},u) = \rho_{\mathrm{X}}(\mathbf{r},0) + \frac{1}{2!}\rho_{\mathrm{X}}^{(2)}(\mathbf{r},0)u^2 + \frac{1}{4!}\rho_{\mathrm{X}}^{(4)}(\mathbf{r},0)u^4 + \cdots . \tag{1}$$

The series expansion does not have odd orders since these contributions vanish in the spherical average. Equation (1) is a key tool for the development of approximate exchange functionals. The LSD approximation to $\rho_{\mathrm{X}}(\mathbf{r},u)$ correctly reproduces the zero-order term in this expansion. GGAs (such as the PBE functional [25]) implicitly aim at [13] reproducing the zero- and second-order term of this expansion in a system-averaged sense. The Becke-Roussel model [23] for $\rho_{\mathrm{X}}(\mathbf{r},u)$ is constructed such that the zero- and second-order terms of Eq. (1) are exactly reproduced, resulting in a simple and accurate approximation to the exchange energy.

Given the success of the Becke-Roussel model, it is tempting to build on this approach and to further pursue the Taylor-series expansion to include the fourth-order term of Eq. (1). We show that the fourth-order term provides important additional features of the exchange hole that can lead to improvements in models for $\rho_{\mathrm{X}}(\mathbf{r},u)$. In more detail, we analyze $\rho_{\mathrm{X}}(\mathbf{r},u)$ for atoms and molecules and find that the fourth-order correction is particularly important in molecules. This is in line with the observation that local and semilocal approximations to exchange are less accurate for molecules than for atoms [26]. Building on the analysis of $\rho_{\mathrm{X}}(\mathbf{r},u)$, we employ $\rho_{\mathrm{X}}^{(4)}(\mathbf{r},0)$ as an ingredient in approximations and we explore its potential to improve upon existing functionals. A somewhat unexpected problem that hampers the use of $\rho_{\mathrm{X}}^{(4)}(\mathbf{r},0)$ is its strong basis set dependence. Conventional Gaussian basis sets [27] provide only a poor representation of this quantity, rendering the use of $\rho_{\mathrm{X}}^{(4)}(\mathbf{r},0)$ for the construction of approximate exchange holes very difficult.

The paper is organized as follows. In Sec. II we introduce theoretical concepts relevant for the exchange hole. Subsequently, in Sec. III we analyze the Taylor series expansion of the spherically averaged hole. Then, in Sec. IV we review the Becke-Roussel model and show how the fourth-order derivative can be used within the BR model. Finally, in Sec. V the conclusions are drawn.

II. EXCHANGE HOLE AND ITS TAYLOR-SERIES EXPANSION

In the KS formalism, the exact exchange energy $E_{\mathrm{X}\sigma}$ of electrons with spin σ is given by

$$E_{\mathrm{X}\sigma}[\rho_\sigma] = -\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{|\gamma_{1\sigma}(\mathbf{r},\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}, \tag{2}$$

where $\gamma_{1\sigma}(\mathbf{r},\mathbf{r}')$ is the one-particle spin-density matrix defined in terms of real occupied KS orbitals as

$$\gamma_{1\sigma}(\mathbf{r},\mathbf{r}') = \sum_{i=1}^{occ}\psi_{i\sigma}(\mathbf{r})\psi_{i\sigma}(\mathbf{r}'). \tag{3}$$

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In KS theory the exchange energy is usually approximated through a density functional. To obtain approximate density functionals, the exchange energy is often first expressed in terms of the exchange hole $\rho_{\mathrm{X}\sigma}(\mathbf{r},\mathbf{r}')$,

$$E_{\mathrm{X}\sigma}[\rho_\sigma] = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{\rho_\sigma(\mathbf{r})\rho_{\mathrm{X}\sigma}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \tag{4}$$

where $\rho_\sigma(\mathbf{r})$ is the σ-spin density at the reference point $\mathbf{r}$. The exchange hole $\rho_{\mathrm{X}\sigma}(\mathbf{r},\mathbf{r}')$ is defined by

$$\rho_{\mathrm{X}\sigma}(\mathbf{r},\mathbf{r}') = -\frac{|\gamma_{1\sigma}(\mathbf{r},\mathbf{r}')|^2}{\rho_\sigma(\mathbf{r})}. \tag{5}$$

Several important properties of the exchange hole can be deduced from Eq. (5) that should be satisfied [11] by models for the hole. First, the exact exchange hole is always negative or zero,

$$\rho_{\mathrm{X}\sigma}(\mathbf{r},\mathbf{r}') \leqslant 0. \tag{6}$$

Similarly, by definition the on-top condition is given by

$$\rho_{\mathrm{X}\sigma}(\mathbf{r},\mathbf{r}) = -\rho_\sigma(\mathbf{r}). \tag{7}$$

As a consequence of the orthonormality of the KS orbitals we obtain the normalization condition,

$$\int d\mathbf{r}'\rho_{\mathrm{X}\sigma}(\mathbf{r},\mathbf{r}') = -1. \tag{8}$$

The exchange hole defined in Eq. (5) is a function of six spatial variables, two of which can be eliminated since the Coulomb potential does only depend on the distance between $\mathbf{r}'$ and $\mathbf{r}$, i.e., on $\mathbf{u} = \mathbf{r}' - \mathbf{r}$, and therefore the spherical average over orientations of $\mathbf{u}$ can be performed,

$$\rho_{\mathrm{X}\sigma}(\mathbf{r},u) = \frac{1}{4\pi}\int_0^{2\pi} d\phi_u \int_0^{\pi} d\theta_u \sin\theta_u\, \rho_{\mathrm{X}\sigma}(\mathbf{r},\mathbf{r}+\mathbf{u}). \tag{9}$$

For later reference, we express the exchange energy per particle in terms of the exchange hole,

$$\epsilon_{\mathrm{X}\sigma}(\mathbf{r}) = \int du\, 4\pi u^2 \frac{\rho_{\mathrm{X}\sigma}(\mathbf{r},u)}{2u} = 2\pi\int du\, u\rho_{\mathrm{X}\sigma}(\mathbf{r},u). \tag{10}$$

$\epsilon_{\mathrm{X}\sigma}(\mathbf{r})$ is related to the exchange energy by

$$E_{\mathrm{X}\sigma}[\rho_\sigma] = \int d^3r\, \rho_\sigma(\mathbf{r})\epsilon_{\mathrm{X}\sigma}(\mathbf{r}). \tag{11}$$

The expansion of Eq. (1) is equivalent to the one introduced by Becke [22,23],

$$\rho_{\mathrm{X}\sigma}(\mathbf{r},u) = \left(1 + \frac{1}{3!}u^2\nabla^2_{\mathbf{r}'} + \frac{1}{5!}u^4\nabla^4_{\mathbf{r}'} + \cdots\right)\rho_{\mathrm{X}\sigma}(\mathbf{r},\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}}, \tag{12}$$

which provides explicit expressions for the calculation of the series coefficients. The zeroth-order term in Eq. (12) is given by

$$\rho_{X\sigma}(\mathbf{r},\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}} = -\rho_\sigma(\mathbf{r}). \tag{13}$$

The second-order term is well known from the work of Becke and Roussel [23],

$$\begin{aligned}\frac{1}{3!}\nabla^2_{\mathbf{r}'}\rho_{X\sigma}(\mathbf{r},\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}} &= -\frac{1}{6}\left[\nabla^2\rho_\sigma - 2\tau_\sigma + \frac{1}{2}\frac{(\boldsymbol{\nabla}\rho_\sigma)^2}{\rho_\sigma}\right]\\ &= -Q_\sigma.\end{aligned} \tag{14}$$

In this expression, the kinetic-energy density τ_σ is given by

$$\tau_\sigma(\mathbf{r}) = \sum_{i=1}^{occ} \boldsymbol{\nabla}_{\mathbf{r}}\psi_{i\sigma}(\mathbf{r})\cdot\boldsymbol{\nabla}_{\mathbf{r}}\psi_{i\sigma}(\mathbf{r}). \tag{15}$$

Note that $\tau_\sigma(\mathbf{r})$ integrates to twice the kinetic energy of the given spin channel. The fourth-order term is evaluated in this work (details are provided in Appendix A) to yield

$$\begin{aligned}\frac{1}{5!}\nabla^4_{\mathbf{r}'}\rho_{X\sigma}(\mathbf{r},\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}} = &-\frac{1}{120\rho_\sigma}\Bigg\{2\rho_\sigma\sum_i^{occ}\psi_{i\sigma}\nabla^4\psi_{i\sigma} + 4\boldsymbol{\nabla}\rho_\sigma\\ &\cdot\sum_i^{occ}\psi_{i\sigma}\nabla^3\psi_{i\sigma} + \frac{1}{2}(\nabla^2\rho_\sigma - 2\tau_\sigma)^2\\ &+4\sum_i^{occ}\psi_{i\sigma}\boldsymbol{\psi}^{(v6)}_{i\sigma}\cdot\sum_j^{occ}\psi_{j\sigma}\boldsymbol{\psi}^{(v6)}_{j\sigma}\Bigg\}\\ =&-T_\sigma,\end{aligned} \tag{16}$$

where

$$\boldsymbol{\psi}^{6v} = (\psi_{xx},\psi_{yy},\psi_{zz},\sqrt{2}\psi_{xy},\sqrt{2}\psi_{xz},\sqrt{2}\psi_{yz}) \tag{17}$$

is a six-dimensional vector (see Appendix A). The subscripts indicate that derivatives with respect to the shown coordinates have been taken.

There are limits and systems for which the rather complicated fourth-order term simplifies. One such limit is the one-electron limit, where the only occupied orbital is equal to the square root of the density. In this case Eq. (16) simplifies to

$$T_\sigma = \frac{1}{120}\nabla^4\rho_\sigma, \quad \text{one electron limit.} \tag{18}$$

This expression is a direct corollary of Eq. (12) and the fact that, for one electron, $\rho_{X\sigma}(\mathbf{r},\mathbf{r}') = -\rho_\sigma(\mathbf{r}')$. Often there is only one orbital contributing to the asymptotic density [28] far away from the nuclei of a molecule. In these cases, Eq. (18) describes the asymptotic form of the fourth-order term.

Another limit in which the fourth derivative simplifies is the homogeneous limit. The derivatives of the density vanish and we obtain

$$\begin{aligned}T_\sigma = \frac{1}{120\rho_\sigma}\Bigg\{&2\rho_\sigma\sum_i^{occ}\psi_{i\sigma}\nabla^4\psi_{i\sigma} + 2\tau_\sigma^2 + 4\sum_i^{occ}\psi_{i\sigma}\boldsymbol{\psi}^{(v6)}_{i\sigma}\\ &\cdot\sum_j^{occ}\psi_{j\sigma}\boldsymbol{\psi}^{(v6)}_{j\sigma}\Bigg\}, \quad \text{homogeneous limit.}\end{aligned} \tag{19}$$

Equation (19) can be further evaluated by introducing the explicit form of the orbitals in the homogeneous electron gas limit (see Appendix B).

The Taylor expansion of $\rho_{\mathrm{X}\sigma}(\mathbf{r},u)$ provides a series that is not necessarily convergent [12]. The molecular orbitals exhibit a cusp at the positions of the nuclei. As a consequence, $\rho_{\mathrm{X}\sigma}(\mathbf{r},u)$ is not an analytic function of the coordinate u and the Taylor series cannot reproduce the cusps. Therefore, one can only hope that the series expansion describes the exchange hole for sufficiently small u values,

$$u < |\mathbf{R}_i - \mathbf{r}|, \tag{20}$$

where $\mathbf{R}_i$ is the position of the nucleus nearest to the reference electron at $\mathbf{r}$. In the present work, Gaussian basis sets are used to expand the orbitals and therefore there are no true nuclear cusps. Formally, the Taylor series should therefore be convergent. However, one would also expect that very high-order terms are needed to capture the cusplike behavior in $\rho_X(\mathbf{r},u)$ if relation (20) is violated.

III. ANALYZING THE FOURTH-ORDER TAYLOR EXPANSION OF $\rho_{X\sigma}(\mathbf{r},u)$

To the best of our knowledge, there are no studies that examine to which degree the fourth-order Taylor-series expansion can capture the exchange hole. Therefore, for the present work we implement $\rho_X(\mathbf{r},u)$ in the Gaussian program system [29]. Our implementation, outlined in Appendix C, enables us to represent $\rho_X(\mathbf{r},u)$ on a grid in the $\mathbf{r}$ and u variable and to study the interpolations generated from the grid data. Furthermore, as already mentioned, we also implement the Taylor-series expansion of Eq. (16) up to fourth order (Appendix A) and we can thus compare the spherically averaged hole to its series expansion of increasing order.

The calculations reported in the following sections are performed with a modified version of the Gaussian program system [29]. All molecular geometries have been optimized with the PBE [25] exchange-correlation functional using the 6-311+G(2d,p) basis set [29]. Calculations of total exchange energies and atomization energies have been performed non-self-consistently using converged Hartree-Fock orbitals and the 6-311+G(2d,p) basis set [29] with the "FineGrid" integration option of the Gaussian program system.

First we consider the Be and the N atom. In Figs. 1 and 2 the exact exchange hole at varying reference points is compared to its Taylor-series expansion. As already mentioned, the Taylor expansion is calculated through analytic derivation of the spherically averaged hole. To set the scale for the values of the reference point $\mathbf{r}$, for each atom, the (a) panel shows the radial electron density. The (b) panel shows the hole close to the nucleus where it is mainly located in the 1s shell and where it has a fairly simple shape. In the inset, the hole and its Taylor series are compared. As discussed above, the Taylor expansion is not expected to converge for values of u that are close to or larger than the distance of r to the nearest nucleus. Therefore, the u range of the insets is chosen to be of the order of magnitude of the convergence radius. For the N atom the fourth-order expansion [(b) panel] improves significantly upon the second-order one. For the Be atom [(b) panel] the second- and fourth-order expansion are indistinguishable in the considered u range.

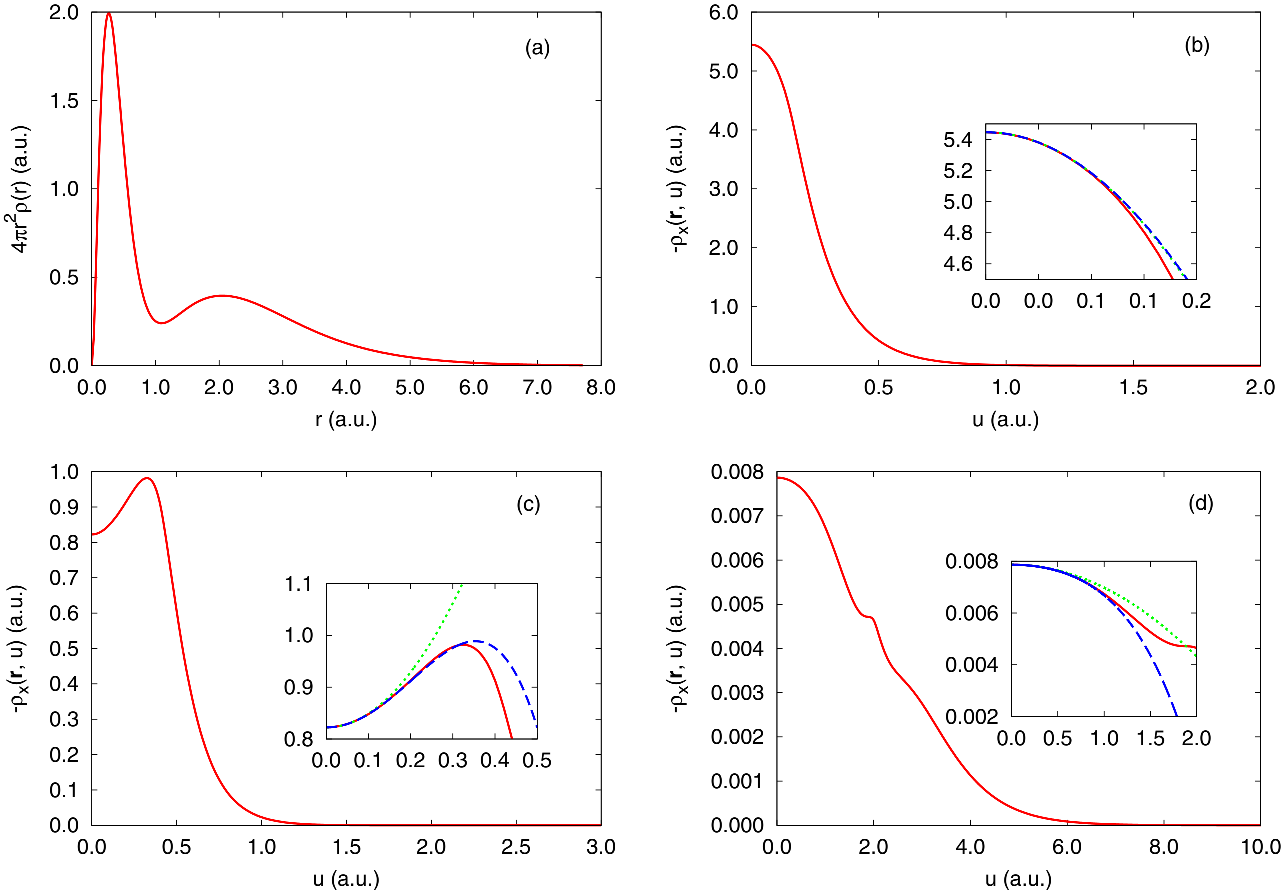

FIG. 1. Comparison of the exchange hole with its Taylor expansion for the Be atom. (a) The radial density of the Be atom. (b)–(d) Comparison of $\rho_X(\mathbf{r},u)$ with its Taylor expansion for various values of $\mathbf{r}$. (b) In the core region $|\mathbf{r}| = 0.15a_0$, (c) in the core-valence region $|\mathbf{r}| = 0.40a_0$, and (d) in the valence region $|\mathbf{r}| = 2.00a_0$. The exchange hole (solid red line), the expansion up to second order (dotted green line), and the expansion up to fourth order (dashed blue line) are shown.

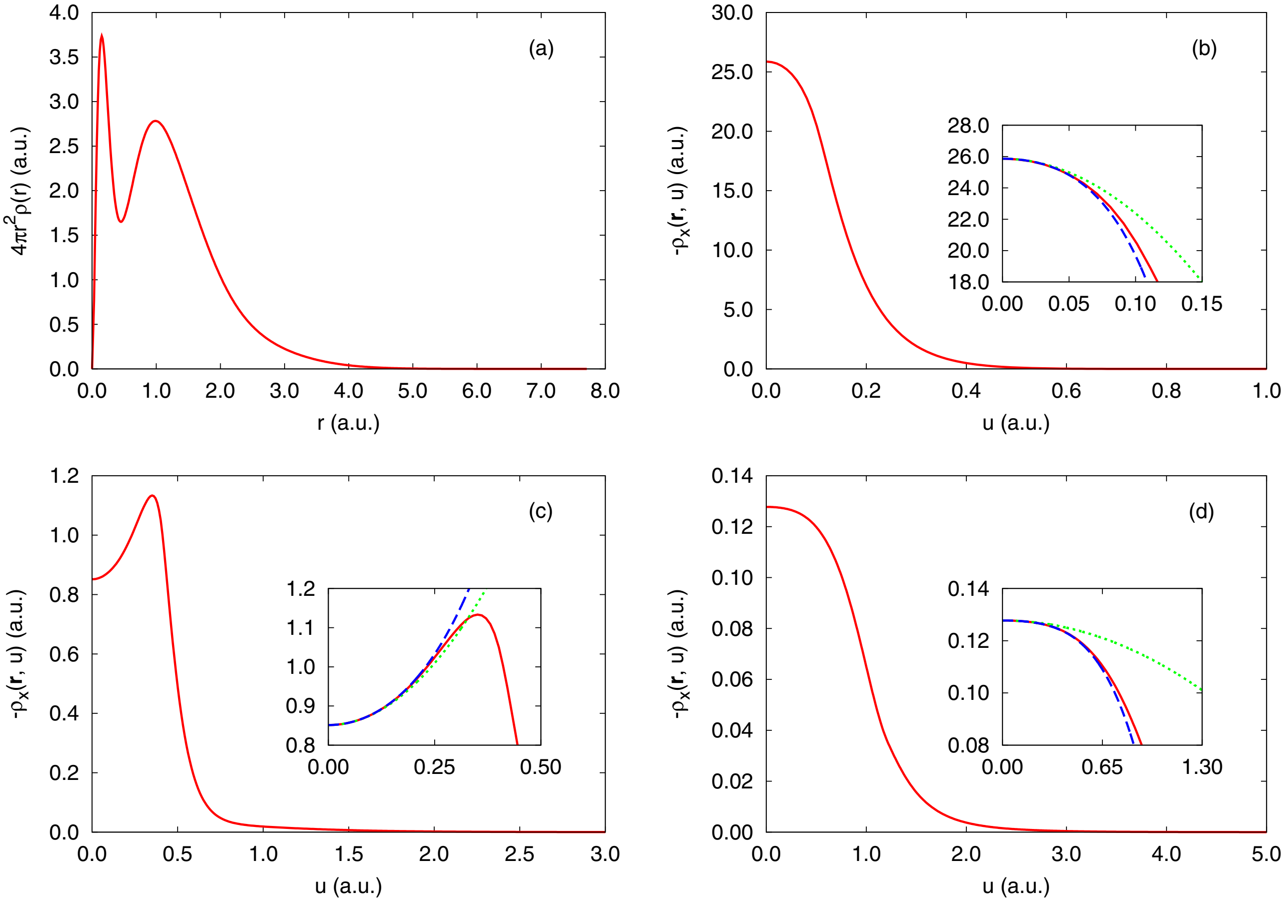

FIG. 2. Comparison of the exchange hole with its Taylor expansion for the N atom. (a) The radial density function of the N atom. (b)–(d) Comparison of $\rho_X(\mathbf{r},u)$ with its Taylor expansion for various values of $\mathbf{r}$. (b) In the core region $|\mathbf{r}| = 0.10a_0$, (c) in the core-valence region $|\mathbf{r}| = 0.40a_0$, and (d) in the valence region $|\mathbf{r}| = 1.25a_0$. The exchange hole (solid red line), the expansion up to second order (dotted green line), and the expansion up to fourth order (dashed blue line) are shown.

Similarly, for r values within the core-valence overlap region [(c) panels], the exchange hole takes on a fairly complex shape. In this case, the fourth-order expansion provides a significant improvement for the Be atom compared to the second-order one. For N, the fourth-order expansion is also more accurate for small u compared to the second-order one. The results for the core-valence region clearly indicate that fourth- and higher-order terms are required to account for the complex shape of the exchange hole. Finally, for a reference point in the valence region [(d) panels], which is of course very important for chemical properties, for both atoms we obtain a significantly improved short-range description through the inclusion of the fourth-order term.

Next we consider the H_2 (Fig. 3) and the N_2 molecule (Fig. 4). The (a) and (b) panels of each plot concern the region between the nuclei and the outside region where both nuclei are on the same side of the reference point, respectively. (In all cases, the reference point is located on the line passing through the nuclei.) In panels (a) and (b), the short-range behavior of the hole is better reproduced by the fourth-order expansion than by the second-order expansion. This is particularly pronounced for N_2. Note that the errors in the exchange energy of N_2, made by functionals such as GGAs and BR, are particularly large compared to the errors made by the same functionals for H_2. This is reflected in the inability of the second-order Taylor representation to capture the short-range behavior of the exchange hole of N_2. Next, in the lower two panels the midbond regions [(c) panels] and also the off-center midbond regions [(d) panels] are examined. In the off-center midbond region, the reference point is displaced perpendicular to the bond axis. In both cases, the fourth-order expansion improves upon the second-order one and this is again particularly pronounced for N_2 where typical local and semilocal exchange functionals perform poorly compared to H_2.

IV. EXCHANGE ENERGY FUNCTIONALS EMPLOYING THE FOURTH-ORDER TAYLOR EXPANSION OF THE EXCHANGE HOLE

A. Becke-Roussel model

The approximate exchange functionals that we use are variations of the Becke-Roussel (BR) model [23] that we summarize first. Becke and Roussel proposed an exchange hole model building on the electron density of a hydrogenic orbital,

$$\rho_\sigma^H(\mathbf{r}) = \frac{\alpha^3}{8\pi} e^{-\alpha r}. \tag{21}$$

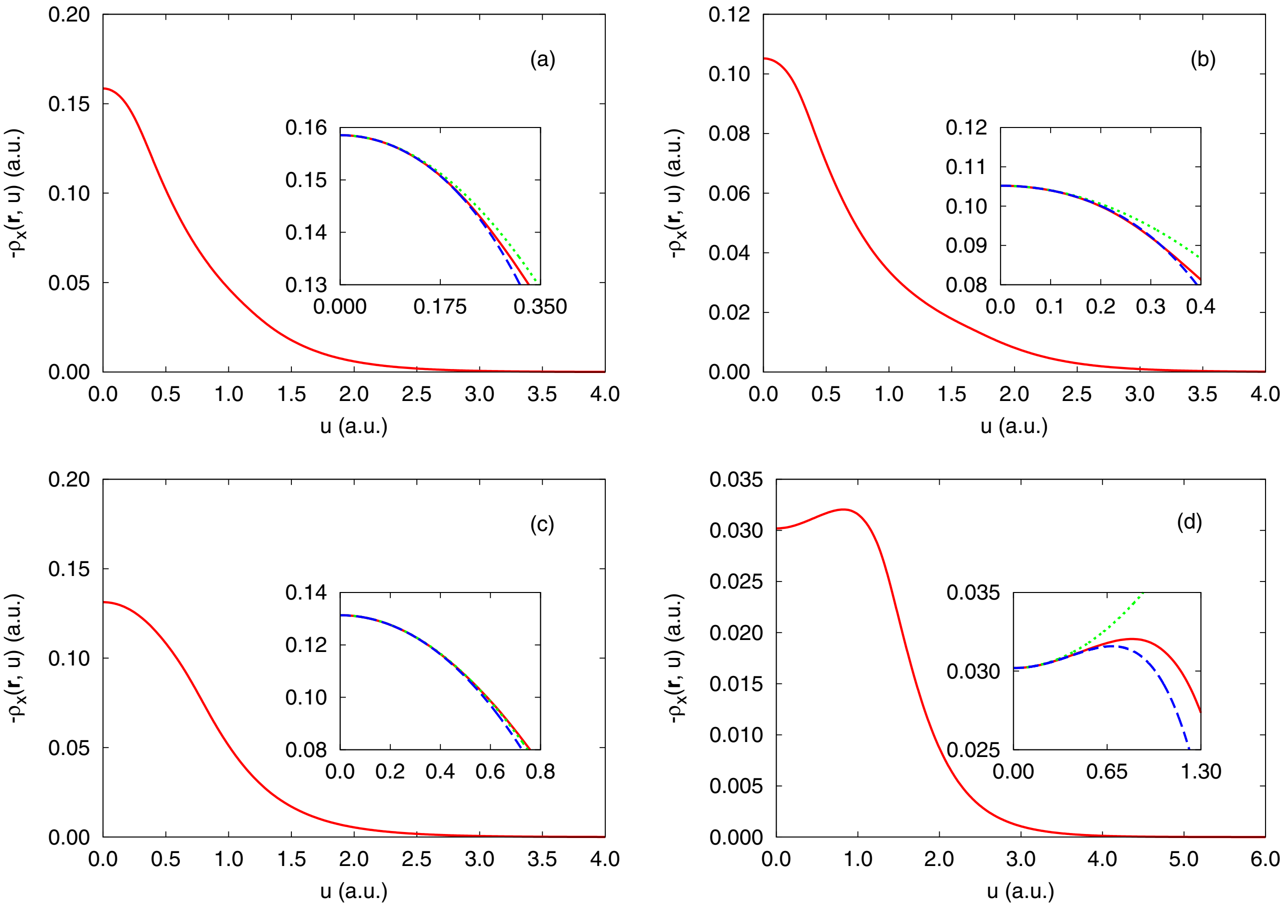

FIG. 3. Comparison of the exchange hole with its Taylor expansion for the H_2 molecule. (a) In the inner core region, where the reference point lies on the bond axis, between the nuclei at a distance of $r = 0.28a_0$, (b) in the outer core region, where the reference point lies on the bond axis on the same side of both nuclei with a distance to the closest one of $r = 0.30a_0$, (c) in the bond midpoint at a distance of $r = 0.72a_0$ from the nuclei, and (d) perpendicular to the bond axis, above the midpoint, at a distance from it of $1.31a_0$. The exchange hole (solid red line), the expansion up to second order (dotted green line), and the expansion up to fourth order (dashed blue line) are shown.

This density is then converted into a spherically averaged hole density $\rho^H_\sigma(\mathbf{r})$,

$$\rho^H_{X\sigma}(\mathbf{r},u) = -\frac{1}{4\pi}\int_0^{2\pi} d\phi_u \int_0^{\pi} d\theta_u \sin_{\theta_u} \rho^H_\sigma(\mathbf{r}+\mathbf{u}) = -\frac{\alpha}{16\pi r u}[(\alpha|r-u|+1)e^{-\alpha|r-u|} - (\alpha|r+u|+1)e^{-\alpha|r+u|}]. \tag{22}$$

Drawing on this expression, Becke and Roussel introduced an exchange-hole model in which α and r are regarded as adjustable parameters and replaced by a and b, respectively,

$$\rho^{BR}_{X\sigma}(a,b,u) = -\frac{a}{16\pi b u}[(a|b-u|+1)e^{-a|b-u|} - (a|b+u|+1)e^{-a|b+u|}]. \tag{23}$$

The values of $a = a(\mathbf{r})$ and $b = b(\mathbf{r})$ are determined as functions of the reference point $\mathbf{r}$ by imposing the condition that the Taylor expansion of $\rho^{BR}_{X\sigma}(a,b,u)$ in powers of u,

$$\rho^{BR}_{X\sigma}(a,b,u) = -\frac{a^3 e^{-ab}}{8\pi} - \frac{a^4(ab-2)e^{-ab}}{48b\pi}u^2 + \cdots , \tag{24}$$

reproduces the expansion of the exact exchange hole up to second order,

$$\rho_{X\sigma}(\mathbf{r},u) = -\rho_\sigma - Q_\sigma u^2 + \cdots . \tag{25}$$

After some algebraic manipulations, two nonlinear equations are obtained:

$$a^3 e^{-ab} = 8\pi\rho_\sigma, \qquad a^2 b - 2a = \frac{6bQ_\sigma}{\rho_\sigma}. \tag{26}$$

Through a variable substitution $x = ab$, it is possible to convert the system of equations (26) into a single equation,

$$\frac{x\, e^{-2x/3}}{(x-2)} = \frac{2\pi^{2/3}}{3}\frac{\rho_\sigma^{5/3}}{Q_\sigma}. \tag{27}$$

This nonlinear equation is usually solved with the Newton-Raphson method at each reference point $\mathbf{r}$. The total exchange energy is given by

$$E_{X\sigma}[\rho_\sigma] = \frac{1}{2}\int d^3r\, \rho_\sigma \epsilon^{BR}_{X\sigma}, \tag{28}$$

where

$$\epsilon^{BR}_{X\sigma} = -\left(1 - e^{-x} - \tfrac{1}{2}xe^{-x}\right)/b. \tag{29}$$

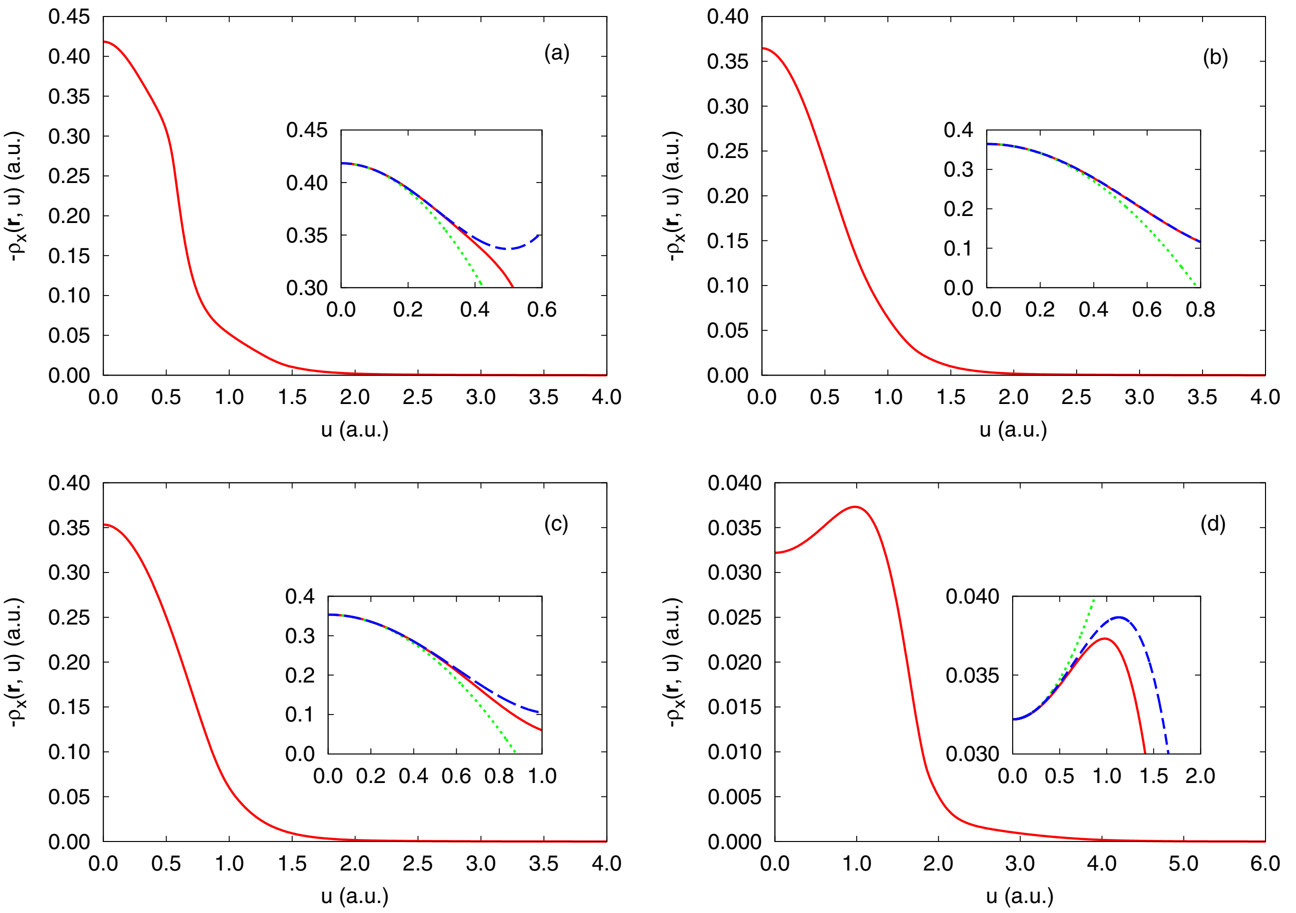

FIG. 4. Comparison of the exchange hole with its Taylor expansion for the N_2 molecule. (a) In the inner-core region $r = 0.55a_0$, (b) at the outer-core region $r = 0.77a_0$, (c) at the bond midpoint with $r = 1.00a_0$, and (d) perpendicular to the bond axis, above the midpoint, at a distance from it of $1.93a_0$. The exchange hole (solid red line), the expansion up to second order (dotted green line), and the expansion up to fourth order (dashed blue line) are shown.

The BR model satisfies important exact constraints, described earlier in Eqs. (6)–(8). In addition, it is exact up to second order in u. Moreover, its exchange energy per particle has the correct asymptotic behavior [30],

$$\lim_{r\to\infty} \epsilon^{BR}_{X\sigma}(r) = -\frac{1}{r}. \tag{30}$$

The success of the BR model can be attributed to the fact that the general form of the exchange hole in atomic systems resembles the hydrogenic hole. The BR model cannot, however, account for very delocalized holes in molecules. Here an attempt is made to lessen this problem. Based on the analysis in the previous section, it appears to be beneficial to use the fourth-order term in the construction of approximate exchange holes. We explored numerous candidates of models that incorporated the fourth-order term; however, we did not succeed in finding an exchange hole model that is flexible enough to reproduce the series expansion of the hole up to fourth order. A factor contributing to this problem is that we use a Gaussian basis set representation of the KS orbitals and this representation introduces large, nonphysical oscillations in the fourth-order term of $\rho_X(\mathbf{r},u)$. This issue is discussed in more detail in Sec. IV B.

To be able to explore functionals of the fourth derivative to a limited extent, we modify the BR construction by replacing the second-order term with the fourth-order term of the Taylor expansion of the exact exchange hole. This results in the following system of equations:

$$\rho^{BR}_{X\sigma}(a,b,u)|_{u=0} = -\rho_\sigma, \tag{31}$$

$$\frac{1}{4!}\frac{d^4}{du^4}\rho^{BR}_{X\sigma}(a,b,u)|_{u=0} = -T_\sigma. \tag{32}$$

Equations (31) and (32) are analogous to Eqs. (24) and (25) of the conventional Becke-Roussel method, the difference being that now the BR exchange hole is constrained to reproduce the exact forth derivative instead of the second-order one. With $x = ab$, Eqs. (31) and (32) can be combined to yield a nonlinear equation in terms of x,

$$\frac{x\,e^{-4x/3}}{(x-4)} = \frac{2\pi^{4/3}}{15}\frac{\rho_\sigma^{7/3}}{T_\sigma}. \tag{33}$$

A plot (Fig. 5) of the right-hand side of Eq. (33) reveals that there is a region to the left of the pole where, for small values of $\frac{2\pi^{4/3}}{15}\frac{R_\sigma^{7/3}}{T_\sigma}$ [the right-hand side of Eq. (33)], there are

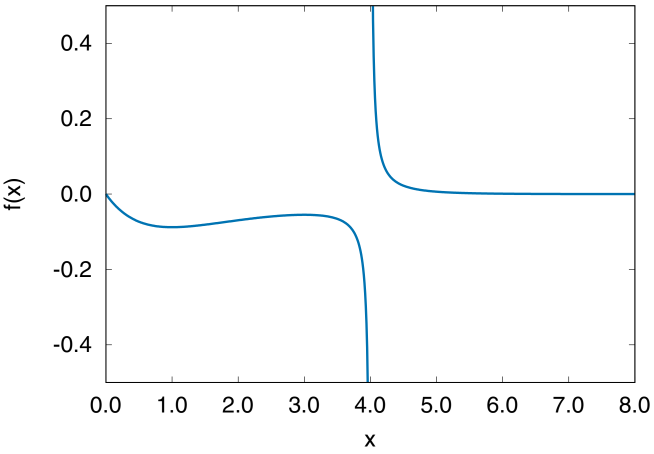

FIG. 5. Graph representing the left-hand side of Eq. (33), i.e., $f(x) = \frac{x\, e^{-4x/3}}{(x-4)}$. For small negative values of $f(x)$, multiple values of x can be found that yield identical $f(x)$.

multiple solutions. To obtain a unique approach, we chose the smallest x value that satisfies Eq. (33). The described procedure determines a and b and, consequently, through Eq. (29), the exchange energy per particle of the BR(4) model $[\epsilon_{X\sigma}^{BR(4)}(\mathbf{r})]$.

B. Gaussian basis set representation of the Taylor-series expansion of $\rho_{X\sigma}(\mathbf{r},u)$

In actual calculations for atoms and molecules, various numerical techniques are employed to facilitate the solution of the KS equations and the calculation of the series expansion of $\rho_{X\sigma}(\mathbf{r},u)$. In the present work, we employ the Gaussian basis set expansions [29] and it is of course important to examine the basis set dependence of the terms in the Taylor series. In particular, the core region requires numerous Gaussian functions with large exponents to ensure an accurate representation of the nuclear cusp. Upon calculating derivatives of the orbitals, the linear combination of the basis functions leads to oscillations and this phenomenon is magnified upon increasing the order of the derivative. Therefore, the fourth-order term is expected to pose a considerable challenge within a basis set approach.

To illustrate this issue, we represent [27] the hydrogen 1s orbital by an increasing number of Gaussian basis functions, plot the fourth-order term of the hole expansion and compare them to the corresponding quantities obtained with the exact exchange hole. In this case we find that increasing the number of basis functions worsens the quality of the representation of the fourth-order term. In particular close to the nucleus, at the origin of the plot, we obtain large errors with the basis set representation. (See Fig. 6.)

C. Combining BR and BR(4)

Having reviewed BR and introduced BR(4), it is tempting to use a position-dependent weighted average of these two approximations. As already explained, we were not yet able to obtain a hole that reproduces the Taylor series up to fourth order but we have one that reproduces the second-order term (BR)) and one that reproduces the fourth-order term [BR(4)]. BR and BR(4) satisfy different constraints whose importance varies as a function of space. Therefore, we combine these two approximations in such a way as to explore their respective strengths. BR works well for atomic densities, in particular it copes with the nuclear cusp, while BR(4) might be more important in the valence region of molecules. A mixed exchange energy per particle that explores the respective strengths is for instance

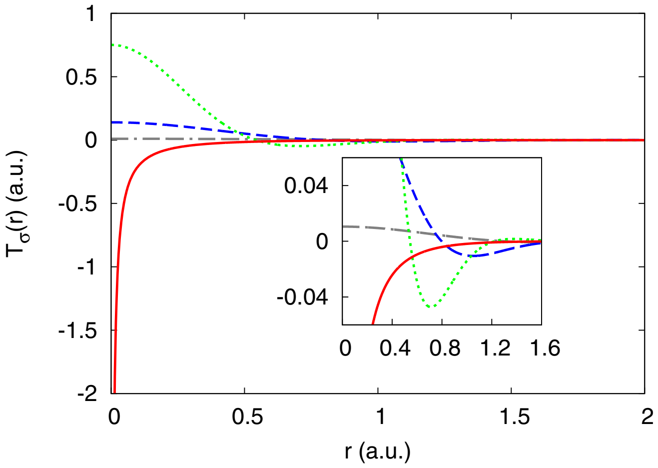

FIG. 6. Exact fourth-order term (solid red line) of a hydrogen atom is compared to the fourth-order term obtained with one (gray dashed-dotted line), two (blue dashed line), and three (green dotted line) Gaussian functions, respectively, which represent the hydrogen orbital [27].

$$\epsilon_{X\sigma}^{h}(\mathbf{r}) = w_\sigma(\mathbf{r})\epsilon_{X\sigma}^{BR(4)}(\mathbf{r}) + [1 - w_\sigma(\mathbf{r})]\epsilon_{X\sigma}^{BR}(\mathbf{r}), \tag{34}$$

where $w_\sigma(\mathbf{r})$ is the mixing fraction with $0 \leqslant w_\sigma(\mathbf{r}) \leqslant 1$. To obtain an *ad hoc* weighting factor, we introduce the dimensionless quantity $\chi_\sigma(\mathbf{r})$,

$$\chi_\sigma(\mathbf{r}) = \left(1 - \frac{2[\tau_\sigma(\mathbf{r}) - 2\tau_{W,\sigma}]}{\nabla^2\rho_\sigma(\mathbf{r})}\right)^2, \tag{35}$$

where $\tau_{W,\sigma} = \frac{[\nabla\rho_\sigma(\mathbf{r})]^2}{8\rho_\sigma(\mathbf{r})}$. Then we define a local mixing function

$$w_\sigma(\mathbf{r}) = e^{-\eta\chi_\sigma(\mathbf{r})}. \tag{36}$$

$\chi_\sigma(\mathbf{r})$ in Eq. (35) reduces to one in the core region where $\tau_\sigma(\mathbf{r}) = 2\tau_{W,\sigma}$ [4]. Away from the core region $\chi_\sigma(\mathbf{r})$ increases further and the weighting factor decreases. The behavior of $w_\sigma(\mathbf{r})$ is illustrated in Fig. 7 where it is plotted for the Be and the N atom. Comparing these plots to the plots of the electron densities of Be and N shows that in the core-valence region $w_\sigma(\mathbf{r})$ drops to zero while it rises again in the valence region. Overall the weighting factor exhibits the desired behavior of being smaller close to the core than in the valence region. We also note that, in the homogeneous limit, $w_\sigma \rightarrow 0$ since $\nabla^2\rho_\sigma(\mathbf{r}) = 0$. Therefore, in the homogeneous limit, we recover BR.

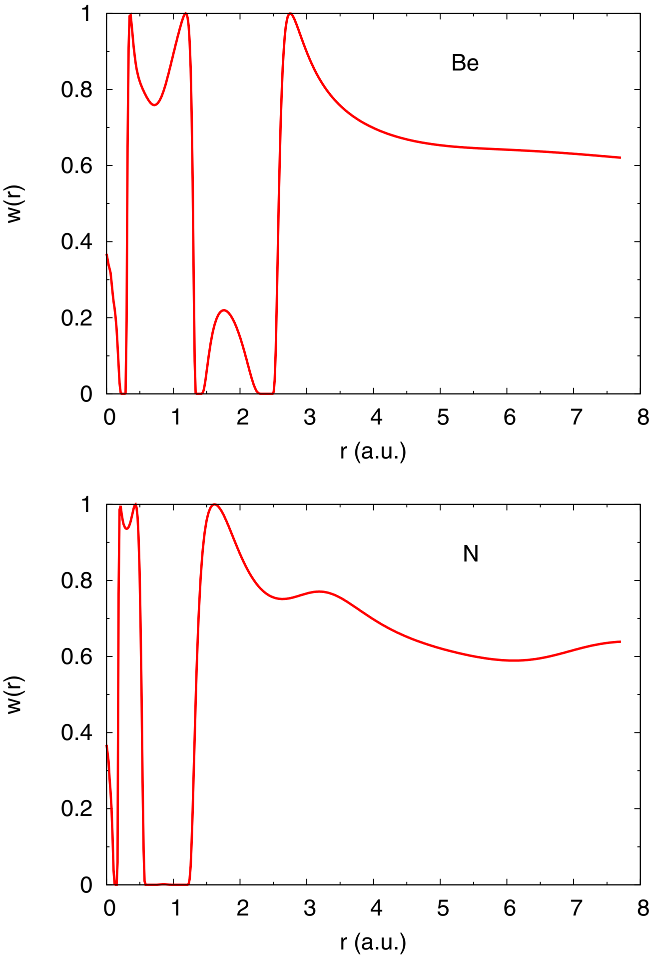

FIG. 7. Mixing coefficient $w(\mathbf{r})$ (with $\eta = 1$) calculated from Hartree-Fock wave functions for the Be (upper panel) and N atom (lower panel).

The hybrid E_X^h [obtained from Eq. (34)] respects the constraints Eqs. (6)–(8) and in an average sense satisfies the second- and fourth-order expansion.

The functionals BR, BR(4), and E_X^h are used to calculate the exchange energies of atoms and molecules which are then compared to the exact as well as PBE [25] exchange results. The parameter η has been optimized for the atomization energies discussed below; the optimal value is $\eta = 36.5$. An interesting observation to make in Table I is that, while the errors for BR(4) are large, they do not increase disproportionately for molecules compared to atoms. Such a disproportionate increase is observed for BR and also for PBE. In the latter case, the exchange energies of atoms tend to be underestimated and the ones of molecules overestimated, so that the relative error by going from atoms to molecules is large. In Table II the exchange contributions to the atomization energy are provided. The hybrid approach E_X^h yields the best performance. On the other hand, the error in the total exchange energies of atoms increases with E_X^h compared to BR and PBE. The hybrid approach presented is not intended to be an approximation for practical use but rather a first exploration of the fourth-order term.

TABLE I. Exchange energies of atoms and molecules (in hartree). The various functionals employed, E_X^{BR}, $E_X^{BR(4)}$, E_X^{PBE}, and E_X^h, are defined in the text. MAE abbreviates mean absolute error. The MAE is calculated for certain subsets as well as for the entire list of systems (total MAE).

Systems	E_X^{Exact}	E_X^{BR}	$E_X^{BR(4)}$	E_X^{PBE}	E_X^h
H	−0.313	−0.313	−0.315	−0.306	−0.313
He	−1.026	−1.039	−1.027	−1.014	−1.036
Li	−1.781	−1.793	−1.778	−1.757	−1.791
Be	−2.666	−2.680	−2.601	−2.635	−2.686
B	−3.768	−3.783	−3.852	−3.731	−3.797
C	−5.074	−5.093	−5.212	−5.030	−5.095
N	−6.603	−6.629	−7.024	−6.549	−6.613
O	−8.210	−8.252	−8.804	−8.165	−8.225
F	−10.035	−10.093	−11.031	−9.995	−10.127
Ne	−12.097	−12.176	−13.596	−12.057	−12.249
Na	−14.015	−14.072	−15.672	−13.947	−14.142
P	−22.641	−22.626	−24.814	−22.503	−22.553
Cl	−27.539	−27.474	−31.705	−27.369	−28.024
MAE	0.000	0.032	0.908	0.055	0.081
H_2	−0.658	−0.658	−0.637	−0.647	−0.652
HF	−10.420	−10.509	−11.577	−10.403	−10.575
Li_2	−3.564	−3.591	−3.576	−3.520	−3.591
LiH	−2.146	−2.165	−2.158	−2.118	−2.168
LiF	−12.008	−11.833	−12.728	−11.703	−11.874
F_2	−19.949	−20.157	−22.030	−19.970	−20.234
Na_2	−28.021	−28.144	−31.368	−27.893	−28.294
Cl_2	−55.092	−54.982	−63.592	−54.781	−56.110
NH_3	−7.665	−7.717	−8.156	−7.631	−7.646
N_2	−13.095	−13.234	−13.888	−13.091	−13.104
O_2	−16.329	−16.504	−17.623	−16.343	−16.397
P_2	−45.201	−45.205	−49.625	−44.973	−45.076
NO	−14.725	−14.875	−15.750	−14.724	−14.769
NO_2	−22.897	−23.166	−24.680	−22.938	−23.032
MAE	0.000	0.110	1.833	0.085	0.166
Total MAE	0.000	0.072	1.387	0.070	0.125

TABLE II. Exchange-energy contributions to atomization energies (ΔE_X) (in hartree). The various functionals employed, E_X^{BR}, $E_X^{BR(4)}$, E_X^{PBE}, and E_X^h, are defined in the text. MAE abbreviates mean absolute error.

Systems	$\Delta E_X^{\text{Exact}}$	ΔE_X^{BR}	$\Delta E_X^{BR(4)}$	ΔE_X^{PBE}	ΔE_X^h
H_2	−0.033	−0.033	−0.006	−0.035	−0.025
HF	−0.073	−0.103	−0.231	−0.103	−0.134
Li_2	−0.003	−0.006	−0.020	−0.006	−0.009
LiH	−0.053	−0.06	−0.065	−0.055	−0.064
LiF	−0.192	0.053	0.080	0.049	0.043
NH_3	−0.125	−0.151	−0.186	−0.165	−0.093
F_2	0.121	0.029	0.031	0.019	0.020
N_2	0.112	0.024	0.160	0.007	0.122
O_2	0.092	0.000	−0.015	−0.013	0.053
P_2	0.082	0.048	0.035	0.032	0.030
NO	0.089	0.006	0.078	−0.011	0.070
NO_2	0.126	−0.033	−0.048	−0.060	0.032
Na_2	0.009	0.000	−0.024	0.001	−0.010
Cl_2	−0.013	−0.034	−0.182	−0.042	−0.061
MAE	0.000	0.064	0.088	0.072	0.053

V. CONCLUSIONS

The main result of the present work is the explicit expression for, and the implementation of, the fourth-order term of the series expansion of $\rho_{\mathrm{X}}(\mathbf{r},u)$ in powers of u. Using this term, we perform an analysis of the expansions of $\rho_{\mathrm{X}}(\mathbf{r},u)$ of second and fourth order. This analysis supports the claim that, in addition to the second-order expansion, the fourth-order one provides important information. This is particularly so for molecules, where the exchange hole is known [13] to be more delocalized and complex in comparison to atoms. In this context it is worth mentioning that (see, e.g. [26,31]) conventional local and semilocal functionals as well as BR make large errors for the exchange energies of molecules compared to atoms. Therefore, the conclusions drawn from the series expansion of the exchange hole are consistent with the problems encountered with local and semilocal functionals. The fourth-order term can potentially eliminate the bias towards atoms in approximate functionals. However, it turned out to be a considerable challenge to develop model holes that reproduce the series expansion up to fourth order. One aspect which aggravates this problem is the poor representation of the fourth-order term through Gaussian basis sets in the core region of atoms and molecules. Close to the core, the **r** dependence of the fourth-order derivative of the exchange hole exhibits strong oscillations. Note, however, that the u dependence of the exchange hole in the chemically relevant regions is well captured by Gaussian basis sets. To the best of our knowledge, no findings to the contrary have been reported. In fact, we show that the fourth-order derivative is very useful to improve the description of the u dependence of the exchange hole. In the absence of a suitable model hole to recover the fourth-order expansion, we employ BR and extend it to BR(4). While this is not completely satisfactory since BR(4) does not recover the second-order term but only the fourth-order one, it enables us to explore the potential of the fourth-order term in a limited fashion by combining the favorable properties of BR and BR(4). To this end, we introduce a locally weighted average of BR and BR(4). The weighting is done such that BR is dominant in the core region and BR(4) is favored in the valence region. This weighted average enables one to perform calculations for atoms and molecules and it indicates that improved exchange functionals can be obtained by considering the fourth-order derivative in addition to the second-order one. In the future we hope to overcome the described difficulties and to integrate the fourth-order term in exchange functionals in a rigorous manner. Improved exchange functionals could make the exact exchange components of global hybrids unnecessary. This would be of great importance since the calculation of exact exchange is costly, particular in extended systems.

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APPENDIX A: DERIVATION OF THE FOURTH-ORDER TERM IN THE TAYLOR EXPANSION OF $\rho_{\mathrm{X}}(\mathbf{r},u)$

Assuming real valued KS orbitals, the exchange hole can be written as

$$\rho_{\mathrm{X}\sigma}(\mathbf{r}_1,\mathbf{r}_2) = -\frac{1}{\rho_\sigma(\mathbf{r}_1)}\left(\sum_i^{occ}\psi_{i\sigma}(\mathbf{r}_1)\psi_{i\sigma}(\mathbf{r}_2)\right)^2. \tag{A1}$$

The fourth-order term of the Taylor expansion of the spherically averaged exchange hole is given by

$$\begin{aligned}\frac{1}{5!}\nabla^4_{\mathbf{r}_2}\rho_{\mathrm{X}\sigma}(\mathbf{r}_1,\mathbf{r}_2)|_{\mathbf{r}_1=\mathbf{r}_2} &= -\frac{1}{5!\rho_\sigma(\mathbf{r}_1)}\nabla^4_{\mathbf{r}_2}\left(\sum_i^{occ}\psi_{i\sigma}(\mathbf{r}_1)\psi_{i\sigma}(\mathbf{r}_2)\right)^2\Bigg|_{\mathbf{r}_1=\mathbf{r}_2}\\ &= -\frac{1}{5!\rho_\sigma(\mathbf{r}_1)}\sum_{ij}^{occ}\psi_{i\sigma}(\mathbf{r}_1)\psi_{j\sigma}(\mathbf{r}_1)\nabla^4_{\mathbf{r}_2}\psi_{i\sigma}(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_2)|_{\mathbf{r}_1=\mathbf{r}_2}\\ &= -T_\sigma(\mathbf{r}).\end{aligned} \tag{A2}$$

Since

$$\begin{aligned}&\nabla^4_{\mathbf{r}_2}\psi_{i\sigma}(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_2)\\ &\quad= \nabla^2_{\mathbf{r}_2}\sum_{ij}^{occ}\Big(\psi_{i\sigma}(\mathbf{r}_2)\nabla^2_{\mathbf{r}_2}\psi_{j\sigma}(\mathbf{r}_2) + 2\nabla_{\mathbf{r}_2}\psi_{i\sigma}(\mathbf{r}_2)\cdot\nabla_{\mathbf{r}_2}\psi_{j\sigma}(\mathbf{r}_2) + \psi_{j\sigma}(\mathbf{r}_2)\nabla^2_{\mathbf{r}_2}\psi_{i\sigma}(\mathbf{r}_2)\Big),\end{aligned} \tag{A3}$$

the explicit form of T_σ at the coalescence point $\mathbf{r}_2 = \mathbf{r}_1$ becomes (omitting $\mathbf{r}_1$ for brevity)

$$T_\sigma = \frac{1}{5!\rho_\sigma}\sum_{ij}^{occ}\psi_{i\sigma}\psi_{j\sigma}\{\psi_{i\sigma}\nabla^4\psi_{j\sigma} + 4\nabla\psi_{i\sigma}\cdot\nabla^3\psi_{j\sigma} + 2\nabla^2\psi_{j\sigma}\nabla^2\psi_{i\sigma} + \psi_{j\sigma}\nabla^4\psi_{i\sigma} + 4\nabla\cdot((\nabla\psi_{j\sigma}\cdot\nabla)\nabla\psi_{i\sigma})\}. \tag{A4}$$

The last term in Eq. (A4) can be simplified if we define a six-dimension vector,

$$\boldsymbol{g}^{(v6)} = (g_{xx}, g_{yy}, g_{zz}, \sqrt{2}g_{xy}, \sqrt{2}g_{xz}, \sqrt{2}g_{yz}), \tag{A5}$$

where the subscripts in the functions g denote derivations with respect to the coordinates. Using Eq. (A5) we have

$$\nabla \cdot ((\nabla g \cdot \nabla)\nabla f) = \boldsymbol{g}^{(v6)} \cdot \boldsymbol{f}^{(v6)} + \nabla g \cdot \nabla^3 f. \tag{A6}$$

Therefore, rearranging the terms in Eq. (A4) and using Eq. (A6), we obtain the fourth-order term of the Taylor expansion of the exact spherically averaged exchange hole,

$$T_\sigma = \frac{1}{5!\rho_\sigma}\left\{2\rho_\sigma \sum_j^{occ} \psi_{j\sigma}\nabla^4\psi_{j\sigma} + 4\nabla\rho_\sigma \cdot \sum_j^{occ} \psi_{j\sigma}\nabla^3\psi_{j\sigma} + \frac{1}{2}(\nabla^2\rho_\sigma - 2\tau_\sigma)^2 + 4\sum_i^{occ} \psi_{i\sigma}\boldsymbol{\psi}_{i\sigma}^{(v6)} \cdot \sum_j^{occ} \psi_{j\sigma}\boldsymbol{\psi}_{j\sigma}^{(v6)}\right\}. \tag{A7}$$

APPENDIX B: FOURTH-ORDER TERM IN THE HOMOGENEOUS ELECTRON GAS LIMIT

In the homogeneous electron gas limit all derivatives of the density vanish and the sums over the occupied orbitals become integrals over the wave vector $\boldsymbol{k}$ up to the Fermi level [6]. Our derivation of the fourth-order term, displayed in Eq. (16), assumes that the orbitals are real. Therefore, instead of using plane waves as orbitals in the homogeneous limit, we replace them by sin- and cos-type orbitals, which are linear combinations of plane waves,

$$\begin{aligned}\psi_c(\boldsymbol{k},\mathbf{r}) &= \frac{1}{2\sqrt{(2\pi)^3}}[e^{i\boldsymbol{k}\cdot\mathbf{r}} + e^{-i\boldsymbol{k}\cdot\mathbf{r}}]\\ &= \frac{1}{\sqrt{(2\pi)^3}}\cos(\boldsymbol{k}\cdot\mathbf{r}),\end{aligned} \tag{B1}$$

$$\begin{aligned}\psi_s(\boldsymbol{k},\mathbf{r}) &= \frac{1}{2i\sqrt{(2\pi)^3}}[e^{i\boldsymbol{k}\cdot\mathbf{r}} - e^{-i\boldsymbol{k}\cdot\mathbf{r}}]\\ &= \frac{1}{\sqrt{(2\pi)^3}}\sin(\boldsymbol{k}\cdot\mathbf{r}).\end{aligned} \tag{B2}$$

Thus the fourth-order term in Eq. (19) reduces to

$$\begin{aligned}T_\sigma(\mathbf{r}) = \frac{1}{240\rho_\sigma(\mathbf{r})}\bigg\{&\rho_\sigma(\mathbf{r})\int_0^{k_F} d\boldsymbol{k} \sum_{i=s,c} \psi_{i\sigma}(\boldsymbol{k},\mathbf{r})\nabla_{\mathbf{r}}^4\psi_{i\sigma}(\boldsymbol{k},\mathbf{r}) + \int_0^{k_F} d\boldsymbol{k}\, \tau_\sigma^2(\boldsymbol{k},\mathbf{r})\\ &+ 2\int_0^{k_F} d\boldsymbol{k} \sum_{i=s,c} \psi_{i\sigma}(\boldsymbol{k},\mathbf{r})\boldsymbol{\psi}_{i\sigma}^{(v6)}(\boldsymbol{k},\mathbf{r}) \cdot \int_0^{k_F} d\boldsymbol{k} \sum_{i=s,c} \psi_{i\sigma}(\boldsymbol{k},\mathbf{r})\boldsymbol{\psi}_{i\sigma}^{(v6)}(\boldsymbol{k},\mathbf{r})\bigg\}.\end{aligned} \tag{B3}$$

This formula can be further evaluated with symbolic mathematics software and a cumbersome expression is obtained that we do not reproduce here.

APPENDIX C: CALCULATION OF THE SPHERICALLY AVERAGED EXCHANGE HOLE IN A GAUSSIAN BASIS SET

Starting from the definition of the exchange hole in Eq. (A1), we derive the working equation of the spherical average exchange hole $\rho_{X\sigma}(\mathbf{r}_1,u)$,

$$\rho_{X\sigma}(\mathbf{r}_1,u) = -\frac{1}{\rho_\sigma(\mathbf{r}_1)}\left(\sum_{ij}^{occ} \psi_{i\sigma}(\mathbf{r}_1)\psi_{j\sigma}(\mathbf{r}_1)\int \frac{d\Omega_u}{4\pi}\psi_{i\sigma}(\mathbf{r}_1+\mathbf{u})\psi_{j\sigma}(\mathbf{r}+\mathbf{u})\right), \tag{C1}$$

where $\mathbf{r}_2 = \mathbf{r}_1 + \mathbf{u}$. $\psi_{i\sigma}$ denotes a molecular orbital that is expanded in primitive Gaussians (χ_p), where the expansion coefficients are the molecular orbital coefficients ($C_{\alpha i}$) and contraction coefficients ($D_{p\alpha}$),

$$\psi_{i\sigma} = \sum_\alpha C_{\alpha i}\phi_\alpha = \sum_{\alpha p} C_{\alpha i} D_{p\alpha}\chi_p. \tag{C2}$$

We consider the terms involving the spherical average separately,

$$Z_{ij}(\mathbf{r}_1,u) = \int \frac{d\Omega_u}{4\pi}\psi_{i\sigma}(\mathbf{r}_1+\mathbf{u})\psi_{j\sigma}(\mathbf{r}_1+\mathbf{u}) = \sum_{\alpha\beta pq} C_{\alpha i}C_{\beta j}D_{p\alpha}D_{q\beta}\int \frac{d\Omega_u}{4\pi}\chi_p(\mathbf{r}_1+\mathbf{u})\chi_q(\mathbf{r}_1+\mathbf{u}). \tag{C3}$$

The spherical averages appearing in this expression are performed analytically as described in [15]. Inserting Eq. (C3) into Eq. (C1), the working equation is obtained,

$$\rho_{X\sigma}(\mathbf{r}_1,u) = -\frac{1}{\rho_\sigma(\mathbf{r}_1)}\sum_{ij}^{occ}\psi_{i\sigma}(\mathbf{r}_1)\psi_{j\sigma}(\mathbf{r}_1)Z_{ij}(\mathbf{r}_1,u). \tag{C4}$$

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