

Charge density reconstitution from approximate exchange-correlation holes

Paola Gori-Giorgi, János G. Ángyán, and Andreas Savin

Abstract: The electronic charge density and the expectation of any one-electronic operator can be reconstructed by a density-weighted integral of the exchange-correlation hole. This property can be used to test and improve approximate holes that are not spherically averaged. As an example, we test the Becke–Roussel exchange-hole model in its nonspherical formulation on small atoms, finding that it accurately reproduces the density in the core region, while missing some of the features of the valence and core-valence regions. The same test on the local-density approximation shows poor results, as expected.

Key words: electronic structure theory, density functional theory, electronic correlations, exchange-correlation functionals, pair-correlation functions.

Résumé : On peut reconstruire la densité de charge électronique et la valeur moyenne des opérateurs monoélectroniques sous forme d'une intégrale du trou d'échange-corrélation pondérée par la densité. Cette propriété peut être utilisée pour tester et améliorer les trous approximatifs qui ne sont pas moyennés selon les directions dans l'espace. Comme exemple, opérant sur de petits atomes, on peut tester le modèle d'échange de trou de Becke–Roussel dans sa formulation non sphérique et on trouve qu'elle reproduit d'une façon précise la densité dans la région de coeur même si l'accord est moins bon dans les régions de valence et de coeur-valence. Tel que prévu, le même test effectué en utilisant l'approximation de densité locale produit des résultats assez médiocres.

Mots-clés : théorie de la structure électronique, théorie de la fonctionnelle de la densité, corrélations électroniques, fonctionnelles d'échange-corrélation, fonctions de corrélation de paires.

Introduction

Density functional theory (DFT)^{1,2} in its Kohn–Sham (KS)³ formulation is nowadays a widely used method in quantum chemistry and solid-state physics, thanks to its unique combination of low computational cost and reasonable accuracy.⁴ In the Kohn–Sham formalism, the total energy of a many-electron system in the external electron-nuclei potential, $\hat{V}_{\text{ne}} = \sum_i v_{\text{ne}}(\mathbf{r}_i)$, is rewritten as a functional of the one-electron density, $\rho(\mathbf{r})$,

$$[1] \quad E[\rho] = T_s[\rho] + U[\rho] + E_{\text{xc}}[\rho] + \int d\mathbf{r} v_{\text{ne}}(\mathbf{r}) \rho(\mathbf{r})$$

In eq. [1], $T_s[\rho]$ is the kinetic energy of a non-interacting system of fermions (usually called the KS system) having the same one-electron density, ρ , of the physical, interacting system. The Hartree energy, $U[\rho]$, is the classical repulsion energy, $U[\rho] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') |\mathbf{r} - \mathbf{r}'|^{-1}$, and the

exchange-correlation functional, $E_{\text{xc}}[\rho]$, must be approximated.

Despite its success, to which can be ascribed the description of a variety of systems, from bulk materials to proteins, KS DFT is still plagued by several unsolved problems. For example, approximate KS DFT has well known problems in handling near-degeneracy effects (rearrangement of electrons within partially filled shells) and in the description of long-range dispersion forces. The quest for better approximations for the exchange-correlation functional, $E_{\text{xc}}[\rho]$, is thus a very active research field (for recent reviews see, e.g., refs. 5–9).

The exchange-correlation (xc) hole has always played a special role in this quest, as a powerful tool to understand^{10–18} and build (see, e.g., refs. 19–27) approximations. In particular, the exact properties of the xc hole have been extensively used to construct nonempirical $E_{\text{xc}}[\rho]$. As we shall review later, to compute the exchange-correlation energy one only needs knowledge of the system- and spheri-

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cally averaged xc hole. Usually, most of the approximations try to construct a model for the spherically averaged hole in each point of space, neglecting those exact properties that do not affect the final system-averaged result (i.e., the final integration over all space). In real systems of nonuniform density, the xc hole can be highly nonspherical (an elegant discussion based on the shape of localized orbitals was given in ref. 11), and one can expect that somehow taking into account this anisotropy would improve the resulting $E_{xc}[\rho]$ and other properties that can be calculated from the xc hole. For example, an interesting recent model for describing van der Waals interactions is precisely based on the anisotropy of the exchange hole.^{28–32}

In this paper, we focus on an exact property (the “charge density reconstitution”) of the (nonspherically averaged) xc hole that is often overlooked (since it does not affect system- and spherically averaged models), by testing some approximate holes on small atoms. After giving the basic definitions in the next section, we analyze the charge density reconstitution in the “charge reconstitution” section, discussing its generalization to one-electron properties. In the “Becke–Roussel exchange hole before spherical average” and “local density approximation” sections, we give two examples of charge density reconstitution for small atoms from the Becke–Roussel²³ exchange hole and the local-density approximation (LDA) xc hole, respectively.

Definitions

Although KS DFT was first formulated as a method “without wavefunction”, writing an expression for the xc functional, $E_{xc}[\rho]$, in terms of wave functions is a useful step to define the xc hole. This can be done via the adiabatic connection formalism.^{10,33–36} In its simplest version,^{10,33,34} the electron–electron repulsion operator, $\widehat{W}_{ee} = \sum_{i=1}^N \sum_{j=i+1}^N 1/|\mathbf{r}_i - \mathbf{r}_j|$, in the N -electron hamiltonian is multiplied by a real parameter, λ , which varies between 0 and 1. At the same time, the physical external potential, $v_{ne}(\mathbf{r})$, is replaced by another local potential, $v^\lambda(\mathbf{r})$, determined by the condition that the one-electron density, $\rho(\mathbf{r})$, does not change with λ . If Ψ^λ denotes the ground state of these λ -dependent hamiltonians, we have the exact formula^{10,34}

$$[2] \quad E_{xc}[\rho] = \int_0^1 \langle \Psi^\lambda | \widehat{W}_{ee} | \Psi^\lambda \rangle d\lambda - U[\rho]$$

This decomposition of $E_{xc}[\rho]$ is by no means unique: for example, one can consider different ways of turning on the electron–electron interaction^{35,36} or a formula that only involves the expectation of the kinetic energy.^{37,38} The simple adiabatic connection that leads to eq. [2] is by far the most used to build approximations.

Introducing the spin-summed pair density, $P_2(\mathbf{r}, \mathbf{r}')$, associated with a given N -electron wave function, Ψ ,

$$[3] \quad P_2(\mathbf{r}, \mathbf{r}') = N(N-1) \times \sum_{\sigma_1, \dots, \sigma_N} \int |\Psi(\mathbf{r}\sigma_1, \mathbf{r}'\sigma_2, \mathbf{r}_3\sigma_3, \dots, \mathbf{r}_N\sigma_N)|^2 d\mathbf{r}_3, \dots, d\mathbf{r}_N$$

we can rewrite eq. [2] as

$$[4] \quad E_{xc}[\rho] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\bar{P}_2(\mathbf{r}, \mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

where

$$[5] \quad \bar{P}_2(\mathbf{r}, \mathbf{r}') = \int_0^1 d\lambda P_2^\lambda(\mathbf{r}, \mathbf{r}')$$

is the coupling-constant-averaged pair density, and P_2^λ is obtained by putting Ψ^λ in eq. [3]. The interaction-averaged xc hole, $h_{xc}(\mathbf{r}, \mathbf{r}')$, is then usually defined as

$$[6] \quad h_{xc}(\mathbf{r}, \mathbf{r}') = \frac{\bar{P}_2(\mathbf{r}, \mathbf{r}')}{\rho(\mathbf{r})} - \rho(\mathbf{r}')$$

so that

$$[7] \quad E_{xc}[\rho] = \frac{1}{2} \int d\mathbf{r} \rho(\mathbf{r}) \int d\mathbf{r}' \frac{h_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Since the xc hole is simply related to the pair density, all its properties come from exact conditions satisfied by the pair density itself.³⁹ The xc hole is often divided into exchange (x) and correlation (c),

$$[8] \quad h_x(\mathbf{r}, \mathbf{r}') = \frac{P_2^{KS}(\mathbf{r}, \mathbf{r}')}{\rho(\mathbf{r})} - \rho(\mathbf{r}')$$

$$[9] \quad h_c(\mathbf{r}, \mathbf{r}') = h_{xc}(\mathbf{r}, \mathbf{r}') - h_x(\mathbf{r}, \mathbf{r}')$$

where $P_2^{KS}(\mathbf{r}, \mathbf{r}')$ is the pair density of the Kohn–Sham system, obtained by putting the Kohn–Sham Slater determinant (i.e., $\Psi^{\lambda=0}$) into eq. [3]. Notice that, because of its definition (eq. [6]), the xc hole is not symmetric in its variables, $h_{xc}(\mathbf{r}, \mathbf{r}') \neq h_{xc}(\mathbf{r}', \mathbf{r})$, but satisfies $\rho(\mathbf{r})h_{xc}(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}')h_{xc}(\mathbf{r}', \mathbf{r})$.

Because the Coulomb interaction, $1/|\mathbf{r} - \mathbf{r}'|$, only depends on the electron–electron distance, to compute $E_{xc}[\rho]$ of eq. [7] we only need the spherical average, $h_{xc}^s(\mathbf{r}, u)$, of the xc hole with respect to the direction of $\mathbf{u} = \mathbf{r} - \mathbf{r}'$,

$$[10] \quad h_{xc}^s(\mathbf{r}, u) = \int h_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u}) \frac{d\Omega_{\mathbf{u}}}{4\pi}$$

so that

$$[11] \quad E_{xc}[\rho] = \frac{1}{2} \int d\mathbf{r} \rho(\mathbf{r}) \int_0^\infty du 4\pi u^2 \frac{h_{xc}^s(\mathbf{r}, u)}{u}$$

We can go one step further, and realize that to compute $E_{xc}[\rho]$ we actually only need the system- and spherically averaged hole,

$$[12] \quad \langle h_{xc}^s(u) \rangle = \int d\mathbf{r} \rho(\mathbf{r}) h_{xc}^s(\mathbf{r}, u)$$

$$[13] \quad E_{xc}[\rho] = \frac{1}{2} \int_0^\infty du 4\pi u^2 \frac{\langle h_{xc}^s(u) \rangle}{u}$$

The most common practice when constructing approximations in DFT is somehow in between eqs. [10] and [12]: most models prefer to build $h_{xc}^s(\mathbf{r}, u)$ (e.g., refs. 23, 26, 40–44), but with the idea in mind that only $\langle h_{xc}^s(u) \rangle$ matters for the exchange-correlation energy, so that exact properties of $h_{xc}^s(\mathbf{r}, u)$ that do not affect $\langle h_{xc}^s(u) \rangle$ can be neglected. One of the reasons to follow this practice is that an approximation defined locally is believed to be automatically size consistent, even if this might not be true in the case of systems with a degenerate ground state.^{45,46}

As we integrate information out, passing from $h_{xc}(\mathbf{r}, \mathbf{r}')$ to $h_{xc}^s(\mathbf{r}, u)$ and then to $\langle h_{xc}^s(u) \rangle$, there are exact properties that do not hold anymore (i.e., they can either be hidden in a very complicated way in the integrated quantities, or may just not be important anymore). For instance, the symmetry property, $\rho(\mathbf{r})h_{xc}(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}')h_{xc}(\mathbf{r}', \mathbf{r})$, does not translate into a simple condition for the spherically averaged hole, $h_{xc}^s(\mathbf{r}, u = |\mathbf{r}' - \mathbf{r}|)$, so that, in general, even for the exact hole we have $\rho(\mathbf{r})h_{xc}^s(\mathbf{r}, |\mathbf{r}' - \mathbf{r}|) \neq \rho(\mathbf{r}')h_{xc}^s(\mathbf{r}', |\mathbf{r} - \mathbf{r}'|)$. When targeting only the spherically and system-averaged hole, $\langle h_{xc}^s(u) \rangle$, the original symmetry in \mathbf{r}, \mathbf{r}' does not play a role anyhow: even if we start from a model hole that does not respect it, the integration over all space cancels the contribution from its antisymmetric part.

Besides the possibility of constructing $E_{xc}[\rho]$, the xc holes, $h_{xc}(\mathbf{r}, \mathbf{r}')$ and $h_{xc}^s(\mathbf{r}, u)$, are interesting quantities per se: they contain chemical information, they can be used to estimate the expectation of two-electron properties, and they define a gauge for the exchange-correlation energy density, $\epsilon_{xc}(\mathbf{r})$,

$$[14] \quad \epsilon_{xc}(\mathbf{r}) = \frac{1}{2} \int_0^\infty du 4\pi u^2 \frac{h_{xc}^s(\mathbf{r}, u)}{u}$$

$$[15] \quad E_{xc}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{xc}(\mathbf{r})$$

The exchange-correlation energy density, $\epsilon_{xc}(\mathbf{r})$, is often used as a starting point to refine approximations.

Charge reconstitution

From the definition of the exchange-correlation hole (eq. [6]) and of the one-electron density,

$$\rho(\mathbf{r}) = \frac{1}{N-1} \int d\mathbf{r}' P_2(\mathbf{r}, \mathbf{r}')$$

one obtains the two sum rules

$$[16] \quad \int d\mathbf{r}' h_{xc}(\mathbf{r}, \mathbf{r}') = -1$$

$$[17] \quad \int d\mathbf{r} \rho(\mathbf{r}) h_{xc}(\mathbf{r}, \mathbf{r}') = -\rho(\mathbf{r}')$$

Equation [16] is the usual xc hole sum rule, satisfied by almost all models. It leads to a corresponding sum rule for the spherically averaged hole,

$$[18] \quad \int_0^\infty du 4\pi u^2 h_{xc}^s(\mathbf{r}, u) = -1$$

The second sum rule, eq. [17], is a simple consequence of the symmetry property, $\rho(\mathbf{r})h_{xc}(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}')h_{xc}(\mathbf{r}', \mathbf{r})$, and shows that the electronic charge density can be reconstructed by a density-weighted integral of the exchange-correlation hole (charge reconstitution). Like the symmetry property from which it is derived, this second sum rule does not translate into a simple condition for the spherically averaged hole, because its information is partially averaged out in the integration over the direction of $\mathbf{u} = \mathbf{r}' - \mathbf{r}$ in eq. [10]. Since most of the approximate holes only try to model $h_{xc}^s(\mathbf{r}, u)$, eq. [17] is often neglected in the literature. Notice that if we consider exchange and correlation separately, we obtain

$$[19] \quad \int d\mathbf{r} \rho(\mathbf{r}) h_x(\mathbf{r}, \mathbf{r}') = -\rho(\mathbf{r}')$$

$$[20] \quad \int d\mathbf{r} \rho(\mathbf{r}) h_c(\mathbf{r}, \mathbf{r}') = 0$$

We can define, for any mono-electronic local operator, $\hat{O} = \sum_i o(\mathbf{r}_i)$, an associated exchange-correlation hole projected property

$$[21] \quad o_{xc}(\mathbf{r}) = - \int d\mathbf{r}' o(\mathbf{r}') h_{xc}(\mathbf{r}, \mathbf{r}')$$

By the virtue of eq. [17], the exchange-correlation hole projected property, $o_{xc}(\mathbf{r})$, weighted by the charge density, $\rho(\mathbf{r})$, leads to the same value as the expectation value of the operator, \hat{O} ,

$$[22] \quad \langle \Psi | \hat{O} | \Psi \rangle = \int d\mathbf{r} \rho(\mathbf{r}) o(\mathbf{r}) = \int d\mathbf{r} \rho(\mathbf{r}) o_{xc}(\mathbf{r})$$

Another way to look at it is that, for any local mono-electronic operator, \hat{O} , there exist an associated “exchange-correlation-hole weighted” operator, $\hat{O}_{xc} = \sum_i o_{xc}(\mathbf{r}_i)$, with $o_{xc}(\mathbf{r})$, given by eq. [21], with the same ground-state expectation value.

For instance, $o(\mathbf{r})$ can be a multipole moment function. In the case of the monopole, i.e., $o(\mathbf{r}) = 1$, one obtains the total number of electrons. For the first order moment, $o(\mathbf{r}) = r_\alpha$, where α denotes a cartesian component, x , y , or z , one has

$$[23] \quad \mu_\alpha = - \int d\mathbf{r} \rho(\mathbf{r}) \int d\mathbf{r}' h_{xc}(\mathbf{r}, \mathbf{r}') r'_\alpha$$

where μ_α denotes a cartesian component of the electronic dipole moment. The corresponding characteristic exchange-correlation weighted function, $D_\alpha(\mathbf{r})$,

$$[24] \quad D_\alpha(\mathbf{r}) = - \int d\mathbf{r}' h_{xc}(\mathbf{r}, \mathbf{r}') r'_\alpha$$

provides the coordinates of the xc hole barycenter (center of charge) belonging to the point \mathbf{r} .³⁰ Thus, eq. [23] tells us that the total electronic dipole moment can be obtained as the weighted sum of the xc hole barycenters. This result can be regarded as a generalization of the Wannier-center decomposition of the polarization,⁴⁷ widely used in the solid-state physics community: the Wannier-center, which is a Dirac-like distribution placed in the barycenters of the localized orbitals, is replaced by a fuzzy distribution of xc hole barycenters.⁴⁸ Similar analysis can be carried out for higher-order multipole moments. Notice that if we consider exchange and correlation separately, we see that eqs. [19]–[20] imply that eqs. [21]–[22] hold as well for the exchange hole alone.

Becke and Johnson^{28,31} have constructed a heuristic model to take into account van der Waals interactions between two subsystems using the square, $d_x^2(\mathbf{r}) = \mathbf{d}_x(\mathbf{r}) \cdot \mathbf{d}_x(\mathbf{r})$, of the dipole moment of the exchange hole plus its reference electron on each subsystem,

$$[25] \quad \mathbf{d}_x(\mathbf{r}) = - \int d\mathbf{r}' h_x(\mathbf{r}, \mathbf{r}') \mathbf{r}' - \mathbf{r} = \mathbf{D}(\mathbf{r}) - \mathbf{r}$$

where here the subscript x stands for exchange hole.

Because of the charge density reconstitution sum rule of eq. [17], the exact $\mathbf{d}_x(\mathbf{r})$ has zero expectation,³⁰

$$[26] \quad \int \rho(\mathbf{r}) \mathbf{d}_x(\mathbf{r}) d\mathbf{r} = 0$$

A density functional approximation for $d_x^2(\mathbf{r})$ has been constructed by Becke and Johnson²⁹ using the Becke–Roussel (BR)²³ exchange-hole model. As briefly reviewed in the next section, the BR exchange-hole model is based on the spherical average of an anisotropic hole. Thus, even if its final outcome is a spherically averaged hole, it is based on the idea that the real hole is nonspherical, and for this reason it can be used to estimate the exchange-hole dipole moment. In this context, it is interesting to check how well the BR model before spherical average satisfies eq. [19]. This is the object of the next section.

The Becke–Roussel exchange hole before spherical average

The BR exchange-hole model²³ is inspired by the exact exchange hole of the hydrogen atom: it places a normalized

exponential at a distance $b(\mathbf{r})$ from the position \mathbf{r} of the σ -spin reference electron (the total exchange hole considered in the previous sections is the sum over the two σ -spin holes, $h_x = h_{x,\uparrow} + h_{x,\downarrow}$),

$$[27] \quad h_{x,\sigma}^{\text{BR}}(\mathbf{r}, \mathbf{r}') = - \frac{a^3(\mathbf{r})}{8\pi} e^{-a(\mathbf{r})|\mathbf{r}' - \mathbf{r} + \mathbf{b}(\mathbf{r})|}$$

The dipole moment of this hole plus its reference electron, evaluated with eq. [25], is simply $\mathbf{b}(\mathbf{r})$.

The final form of the BR model is obtained by taking the spherically averaged with respect to the direction of $\mathbf{u} = \mathbf{r}' - \mathbf{r}$ of eq. [27]. This way, the BR spherically averaged hole only depends on the magnitude $b(\mathbf{r})$ of $\mathbf{b}(\mathbf{r})$. The two parameters $a(\mathbf{r})$ and $b(\mathbf{r})$ are fixed by imposing the exact on-top ($\mathbf{r} \rightarrow \mathbf{r}'$ or $u \rightarrow 0$) depth and curvature,

$$[28] \quad h_{x,\sigma}(\mathbf{r}, u) = -\rho_\sigma + \frac{u^2}{6} \left(2\tau_\sigma - \frac{|\nabla \rho_\sigma|^2}{2} - \nabla^2 \rho_\sigma \right) + O(u^4)$$

where $\rho_\sigma(\mathbf{r})$ is the density of spin- σ electrons and $\tau_\sigma = \sum_i |\nabla \phi_{i,\sigma}|^2$ ($\phi_{i,\sigma}$ are the Kohn–Sham orbitals). The model, thus, provides the magnitude of $\mathbf{b}(\mathbf{r})$ but not its direction, since it is not needed either in the spherically averaged hole or in the Becke–Johnson dispersion model,²⁹ which only uses $b^2(r)$.

In an atom, however, with the BR ingredients, the only possible choice is having $\mathbf{b}(\mathbf{r})$ pointing towards the nucleus. In this case we can thus test without ambiguity how well the BR hole model *before* spherical average satisfies eq. [19]. In a spherical atom, the charge density reconstitution of eq. [19] from the BR hole would read

$$[29] \quad \int d\mathbf{r} \rho(r) \frac{a^3(r)}{8\pi} e^{-a(r)|(b(r)/r-1)\mathbf{r} + \mathbf{r}'} = \rho(r')$$

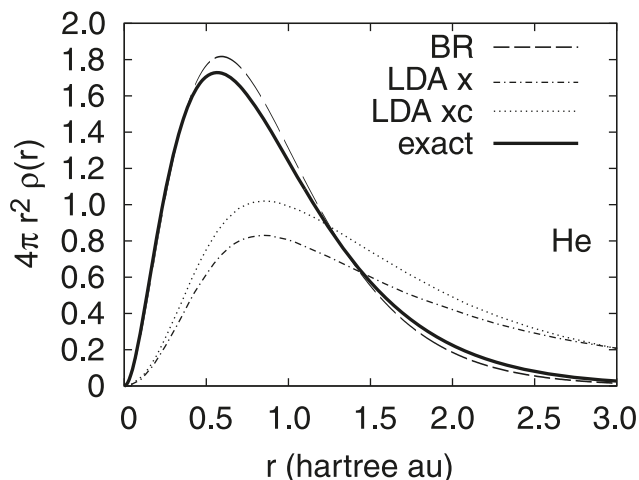
where we now have to check how well this equality is actually satisfied. In the left-hand side of eq. [29], the integration over the angular part of \mathbf{r} is analytical, so that we are left with a one-dimensional integral, which is evaluated numerically on a grid.

In Figs. 1–3, we show our results for the He, Be, and Ne atoms, respectively, using highly accurate input ingredients to avoid any bias (using almost “exact” input quantities allows us to focus on the results of the model, without introducing any other source of error). For the He atom we have used the density coming from the variational wave function of ref. 49, while for Be and Ne we have used the density and the Kohn–Sham orbitals from the accurate Kohn–Sham potentials of refs. 50 and 51. We see that eq. [29] is almost satisfied for the He atom, and for the core region of Be and Ne, which are dominated by $1s$ -type orbitals qualitatively similar to eq. [27]. The valence region of Be, instead, is poorly reproduced, with the BR hole yielding results of similar quality to the LDA (see the next section). Some of the features of the core-valence region of the Ne atom are also missed by the BR hole.

Local density approximation

The local density approximation (LDA) to the exchange-correlation hole consists in taking the xc hole of a uniform

Fig. 1. Charge density reconstitution from approximate holes for the He atom. We tested the Becke–Roussel (BR) exchange hole before spherical average, and the LDA exchange and exchange–correlation hole at full coupling strength.



electron gas with density $\rho(\mathbf{r})$ from around the reference electron at position \mathbf{r} ,

$$[30] \quad h_{xc}^{\text{LDA}}(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}) g_{xc}^{\text{UEG}}(|\mathbf{r}' - \mathbf{r}|; \rho(\mathbf{r}))$$

where $g_{xc}^{\text{UEG}}(u; \rho)$ is the exchange–correlation pair-distribution function (see, e.g., ref. 52). Being that the uniform electron gas is an isotropic system, the LDA xc hole is spherical, and it has been shown to be a surprisingly good approximation for the short-range part (small $u = |\mathbf{r}' - \mathbf{r}|$) of the spherically averaged xc hole of systems of nonuniform density.^{13–15}

As explained in the charge reconstitution section, the sum rule of eq. [17] does not translate into a simple condition on the spherically averaged hole. Thus, if we want to consider LDA as a good approximation for the spherically averaged hole, there is no space for checking eq. [17]. However, since the LDA hole is intrinsically spherical, we can also consider eq. [30] as an approximation for the nonspherically averaged hole. In this case, the charge density reconstitution of eq. [17] for spherical atoms reduces to the condition

$$[31] \quad \rho(r') = 2\pi \int_0^\infty dr r^2 \rho^2(r) \times \int_{-1}^1 dy g_{xc}^{\text{UEG}}(\sqrt{r^2 + r'^2 - 2rr'y}; \rho(r))$$

where again the point is to check whether this equality is actually satisfied. Notice also that other widely used models such as PBE^{40,41} and TPSS⁴² only approximate the spherically averaged hole, so that we cannot carry out similar tests for those models.

Using the same densities of the previous section, we have numerically evaluated the right-hand side of eq. [31] for He, Be, and Ne. We have considered the case of the exchange-only hole and of the exchange–correlation hole at full coupling strength (i.e., with $P_2^{\lambda=1}$ in eq. [6] instead of the coupling-constant averaged \bar{P}_2), using the parametrization of $g_{xc}^{\text{UEG}}(u; \rho)$ of ref. 52. We see from Figs. 1–3 that, as ex-

Fig. 2. Charge density reconstitution from approximate holes for the Be atom. We tested the Becke–Roussel (BR) exchange hole before spherical average, and the LDA exchange and exchange–correlation hole at full coupling strength.

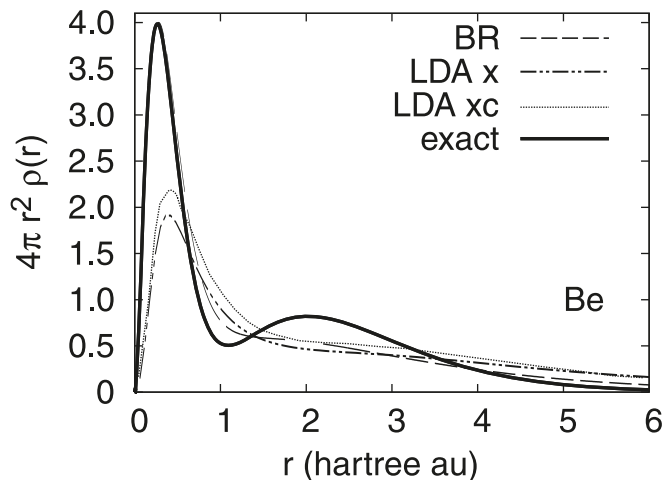
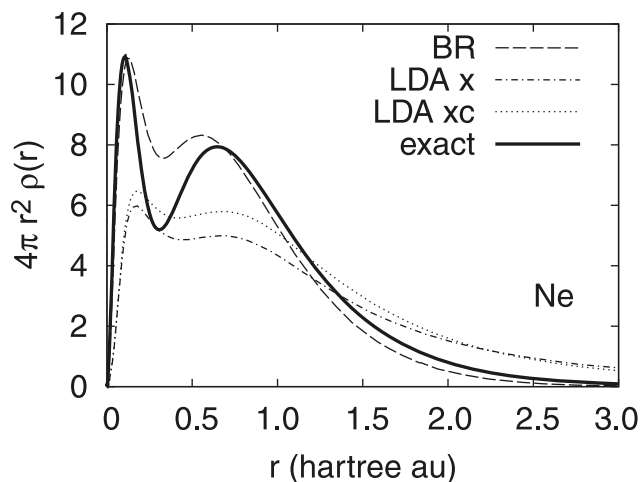


Fig. 3. Charge density reconstitution from approximate holes for the Ne atom. We tested the Becke–Roussel (BR) exchange hole before spherical average, and the LDA exchange and exchange–correlation hole at full coupling strength.



pected, LDA does not satisfy eq. [31], which should actually be fulfilled at the exchange-only level, meaning that adding the correlation part should not change the result. Notice that the curve corresponding to the coupling-constant-averaged xc hole will always lie between the exchange-only result and the full-coupling strength xc result.

This failure of LDA to fulfill eq. [17] should not be considered as a flaw of the model, if we regard LDA as an approximation to the spherically averaged hole, $h_{xc}^s(\mathbf{r}, u)$. As said, the exact spherically averaged hole, $h_{xc}^s(\mathbf{r}, u = |\mathbf{r}' - \mathbf{r}|)$, in fact, is not supposed to satisfy eq. [17] (only the nonspherically averaged hole does). So, if LDA is a reasonable approximation (even if only at short range) for the spherically averaged hole, it should not fulfill eq. [17]. This point is somehow philosophical, since the LDA hole model is exactly the same for the nonspherically averaged $h_{xc}(\mathbf{r}, \mathbf{r}')$ and the spherically averaged $h_{xc}(\mathbf{r}, u)$.

Conclusions and perspectives

We have discussed a sum rule concerning the (nonspherically averaged) exchange-correlation hole, in which different mono-electronic local operators can be used. Even if, eventually, only the system- and spherically averaged hole is needed to obtain the exchange-correlation energy, a given model for the spherically averaged hole (which is interesting by itself to compute different properties and to define energy densities) could be improved by taking into account, in some approximate way, the sum rule of eq. [17]. If the whole eq. [17] may be too hard to impose, a selection of local operators $o(\mathbf{r})$ in eq. [22] might be simpler to handle. For example, the Becke–Roussel²³ hole could be improved by adding some parameters that are adjusted to fulfill, at least approximately, eq. [22] for the case of the dipole moment. This may give a more accurate estimate of the exchange-hole dipole moment needed in the Becke–Johnson model²⁹ for dispersion forces.

Another important point to consider is the following. When dealing with open systems or with systems with strong nondynamical correlation, a better local model for the exchange hole can be obtained by relaxing^{18,27} the sum rule of eq. [16], and thus also, by symmetry, the sum rule of eq. [17] considered here. Again, taking this symmetry into account in some approximate way before the spherical average could also improve a given model for nondynamical correlation.

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