

Influence of the self-interaction error on the structure of the DFT exchange hole

Victor Polo, Jürgen Gräfenstein, Elfi Kraka, Dieter Cremer *

Department of Theoretical Chemistry, Göteborg University, Reutersgatan 2, S-41320 Göteborg, Sweden

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Abstract

Approximate density functional theory (DFT) covers long-range non-dynamic electron correlation via the exchange functional while the correlation functional includes just the short-range dynamic electron correlation effects. We show that the self-interaction error of approximate exchange functionals (local density approximation, LDA and others) mimics the long-range correlation effects. For this purpose the exchange hole is investigated at the Hartree–Fock, the LDA, and the self-interaction corrected (SIC)-LDA levels of theory. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

It is the general understanding that exchange (Fermi) and Coulomb correlation are physically different forms of electron correlation. The first type of correlation affects electrons of equal spin and results from the Pauli exclusion principle. The second effect is a consequence of the Coulomb repulsion law and affects electrons of both spins. An adequate account of both exchange and Coulomb electron correlation is the key to any reliable quantum chemical method. In density functional theory (DFT) exchange correlation is covered by the exchange functional while Coulomb correlation is described by the correlation functional [1]. It is the general understanding that in the latter case just the short-range Coulomb

correlation effects, the so-called dynamic correlation effects, are included. Long-range Coulomb correlation (non-dynamic or static electron correlation), as it occurs in electronic systems with multireference character, is considered not to be adequately described by standard Kohn–Sham DFT when the currently available exchange–correlation functionals are used. Of course, if the correct exchange–correlation functional were known, this would cover beside exchange correlation all short-range and long-range Coulomb correlation effects and would thus give an accurate description of both single and multiple reference systems [1].

In view of the fact that standard DFT is considered to cover just dynamic electron correlation, it performs astonishingly accurately also for electronic systems with some multireference character, for which uncorrelated methods such as Hartree–Fock (HF) fail drastically. In this connection, several authors have pointed out that approximate

* Corresponding author. Fax: +46-31-77-35-590.

E-mail address: cremer@theoc.gu.se (D. Cremer).

exchange in DFT includes long-range (non-dynamic) Coulomb correlation effects [2–6]. This is traced back to the fact that exact HF exchange is considered to be delocalized [7] while DFT operates with strictly local exchange as in the local density approximation (LDA) [8] or at most semilocal exchange as in the generalized gradient approximation [9]. The difference between local exchange and the true delocalized exchange is considered to mimic long-range correlation effects.

In a recent work, we have investigated the electron correlation effects covered by DFT by comparing electron density distributions $\rho(\mathbf{r})$ generated by exchange or exchange-correlation functionals with density distributions obtained from wave function theory methods including well-defined electron correlation effects [10,11]. In this way it was shown that both LDA and GGA exchange functionals describe not only exchange correlation but also Coulomb correlation effects. However, it was also found that the latter are a result of the self-interaction error (SIE) typical of most approximate exchange-correlation functionals. The Coulomb term of the DFT energy, $E_J[\rho]$, includes a self-repulsion part that is only incompletely canceled by the corresponding self-exchange part $E_X[\rho_\sigma, 0]$ (repulsion of the density at a given point \mathbf{r} with itself; σ denotes spin α or β) due to the approximate nature of the exchange functionals used. The resulting SIE separates electrons of a molecule in a fashion that is typical of long-range left–right, angular or in–out correlation. Electron density distributions generated by self-interaction corrected (SIC)-DFT resemble HF densities, i.e. they do not indicate any Coulomb correlation effects beside exchange correlation [10,11].

Although the comparison of electron density distributions generated by DFT with suitable reference densities makes it possible to show Coulomb correlation effects covered by a given functional, it is difficult to distinguish whether a Coulomb correlation effect is caused by short-range (dynamic) or long-range (non-dynamic) electron correlation. For example, a difference electron density distribution $\Delta\rho(\mathbf{r}) = \rho(\text{Method I}) - \rho(\text{Method II})$ generated by second-order Møller–

Plesset (MP2) perturbation theory (Method I) and HF theory (Method II) resembles that generated by Slater-exchange (henceforth called LDA exchange) and HF (see Fig. 1 in the case of H_2 or F_2) although the first is dominated by short-range and the second probably by long-range correlation effects [10,11].

An identification of the type of correlation effects covered by a given exchange functional is possible when the exchange hole [8,12] employed by this functional is investigated. The exchange hole is related to the pair electron density distribution and its structure depends on the location \mathbf{P} of the reference electron. Mathematically, the one-electron density distributions $\rho(\mathbf{r})$, on which our previous investigations were based, are generated from the pair electron density distribution by integration over the coordinates of the reference electron, i.e. one has to sum over a large (actually infinite) number of pictorial representations of the exchange hole for different locations of the reference electron to draw the connection to the difference density distributions such as those shown in Fig. 1. This is probably the reason why pictorial representations of exchange or exchange-correlation holes for molecules are seldom found in the literature. However, as we will show in the following, it suffices to select only a few representative locations \mathbf{P} in a molecule to analyze the difference electron density distributions of Fig. 1 and to connect typical patterns of the latter to the structure of the exchange hole.

In this work, we will demonstrate that the SIE of approximate DFT exchange functional is indeed responsible for long-range correlation effects covered by DFT. We will also show that the SIC-DFT exchange hole is closely related to HF exchange hole and that the SIE restores the local character of DFT exchange. Furthermore, we will discuss the question whether exchange in general may cover long-range Coulomb correlation effects as recently discussed by Handy and Cohen [6].

2. Computational methods

In the case of a single electron with α -spin ($\int \rho_\alpha(\mathbf{r}) d\mathbf{r} = 1$, and $\rho_\beta(\mathbf{r}) = 0$), the correct exchange and correlation functional must lead to an

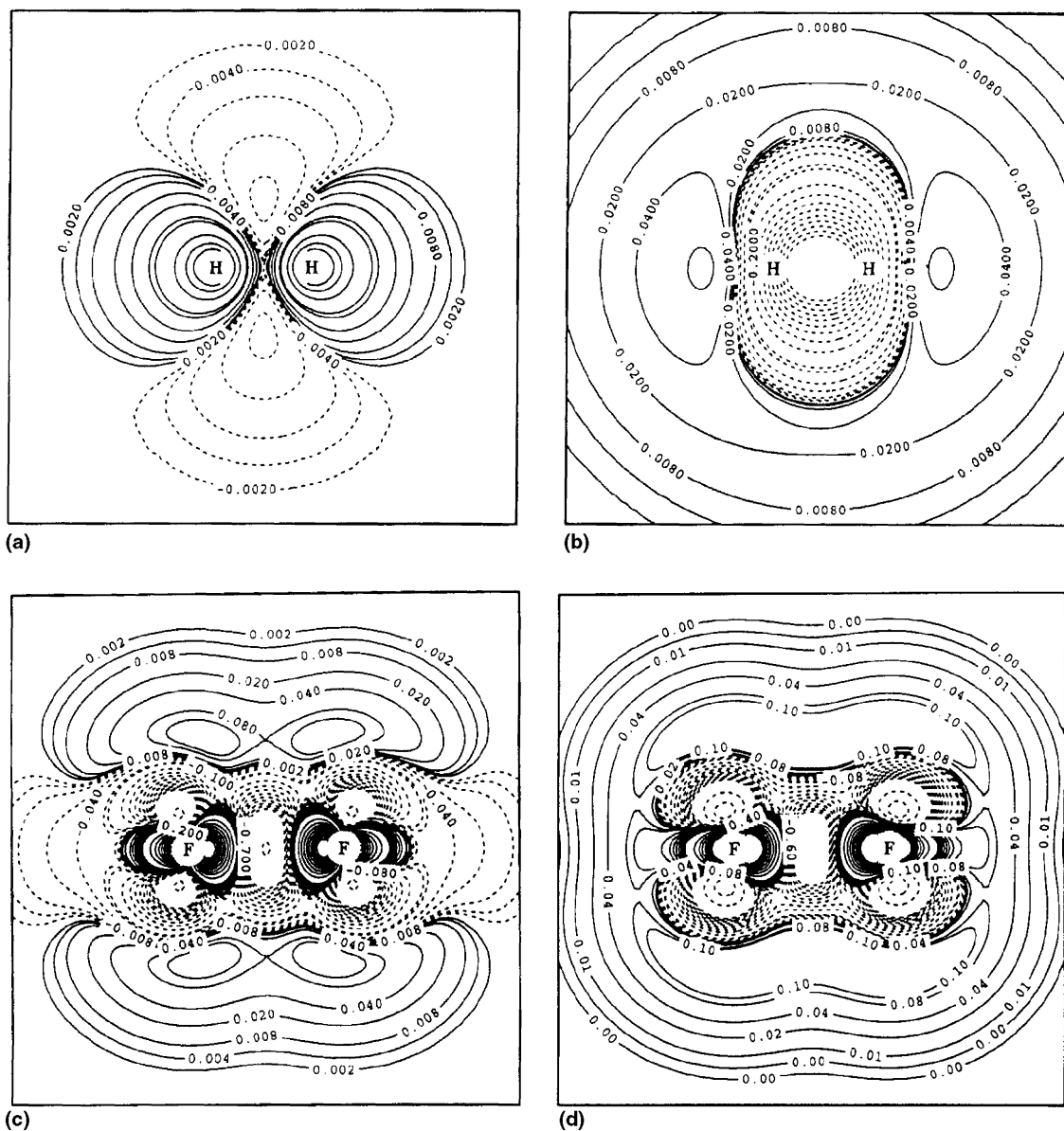


Fig. 1. Contour line diagram of the difference electron density distribution $\Delta\rho(\mathbf{r}) = \rho(\text{Method I}) - \rho(\text{Method II})$ of H_2 , ${}^1\Sigma_g^+$ and F_2 , ${}^1\Sigma_g^+$ calculated with the cc-pVTZ basis at the experimental geometry. Solid (dashed) contour lines are in regions of positive (negative) difference densities. Reference plane is the plane containing the two nuclei. The positions of the atoms are indicated. The contour line levels have to be multiplied by the scaling factor 0.01 and are given in e bohr^{-3} . (a) H_2 : MP2-HF. (b) H_2 : S-only-HF. (c) F_2 : MP2-HF. (d) F_2 : S-only-HF. (S-only denotes DFT calculations with Slater exchange and without correlation functional.)

electron density distribution $\rho_x(\mathbf{r})$ that fulfills Eqs. (1) and (2).

$$E_J[\rho] + E_X[\rho_x, 0] = 0, \quad (1)$$

$$E_C[\rho_x, 0] = 0, \quad (2)$$

which simply mean that a single electron does not interact with itself, i.e. the self-repulsion energy

of the electron given by $E_J[\rho]$ is canceled by the self-exchange energy $E_X[\rho_\alpha, 0]$ covered by the exchange functional. Also, a single electron does not possess any *self-correlation energy* $E_C[\rho_\alpha, 0]$. An approximate XC functional may violate either condition Eqs. (1), (2) or both and, accordingly, self-interaction corrections have to be introduced into DFT to obtain a SIE-free method.

In this work, we use the SIC-DFT approach proposed by Perdew and Zunger [13] to correct the SIE for approximate exchange-correlation functionals orbital by orbital.

$$E_X^{\text{correct}} = E_X^{\text{approx}}[\rho_\alpha, \rho_\beta] - \sum_{\sigma=\alpha,\beta} \sum_i^{N_\sigma} (E_J[\rho_{i\sigma}] + E_X^{\text{approx}}[\rho_{i\sigma}, 0]) = E_X^{\text{approx}}[\rho_\alpha, \rho_\beta] - E_X^{\text{SIC}}, \quad (3)$$

$$E_C^{\text{correct}} = E_C^{\text{approx}}[\rho_\alpha, \rho_\beta] - \sum_{\sigma=\alpha,\beta} \sum_i^{N_\sigma} E_C^{\text{approx}}[\rho_{i\sigma}, 0] = E_C^{\text{approx}}[\rho_\alpha, \rho_\beta] - E_C^{\text{SIC}}. \quad (4)$$

Hence, the electronic energy of SIC-DFT is given by Eq. (5).

$$E^{\text{SIC-DFT}}[\rho] = E_T[\rho] + E_V[\rho] + E_J[\rho] + E_X[\rho] - E_X^{\text{SIC}}[\rho] + E_C[\rho] - E_C^{\text{SIC}}[\rho], \quad (5)$$

where E_T and E_V denote the kinetic energy of non-interacting electrons and the potential energy (nucleus–electron attraction), respectively. The Kohn–Sham equations extended by the Perdew–Zunger SIC-XC functional are solved iteratively with the energy of Eq. (5) being made stationary with regard to a mixing of occupied with occupied and occupied with virtual orbitals [14]. Theory and implementation of a self-consistent SIC-DFT (SCF–SIC-DFT) method is described elsewhere [15]. SCF–SIC-DFT was used in this work to determine the electron density distribution and the exchange hole generated by Slater exchange.

Since SIC-DFT energies and densities require the use of localized orbitals, the latter were also used in the HF and LDA calculations. Using the Boys localization procedure [16], core, bonding and sp^3 -hybridized lone pair orbitals were obtained for F_2 . Because the latter are no longer in-

variant with regard to the mixing between occupied orbitals carried out in the SIC-DFT energy minimization process, only the σ -orbitals of F_2 were localized with the Boys localization procedure for the self-interaction corrections while the π -orbitals were left in their canonical form to keep the molecular symmetry.

The HF exchange hole for a closed-shell system has the form [17]

$$h_X^{\text{HF}}(\mathbf{r}, \mathbf{r} + \mathbf{R}) = -\frac{2}{\rho(\mathbf{r})} \sum_{i,i'} \varphi_i(\mathbf{r})\varphi_i(\mathbf{r} + \mathbf{R}) \times \varphi_{i'}(\mathbf{r})\varphi_{i'}(\mathbf{r} + \mathbf{R}), \quad (6)$$

where \mathbf{r} determines the position of the reference electron; \mathbf{R} denotes the distance between reference electron at \mathbf{r} and the position $\mathbf{r} + \mathbf{R}$ of the second electron. Eq. (6) reflects that exchange reduces the probability of finding two equal-spin electrons at the same position to zero while opposite-spin electrons are unaffected by exchange effects.

The exchange hole can be decomposed into (i) a contribution $h_X^{\text{HF,intra}}$ accounting for the self-exchange of the electrons, which annihilates the self-repulsion part of electron pairs consisting of twice the same electron, and (ii) a contribution $h_X^{\text{HF,inter}}$ that describes the Fermi correlation between different electrons, i.e. accounts for the antisymmetry of the total wave function. It is

$$h_X^{\text{HF,intra}}(\mathbf{r}, \mathbf{r} + \mathbf{R}) = -2 \sum_i \frac{\rho_i(\mathbf{r})}{\rho(\mathbf{r})} \rho_i(\mathbf{r} + \mathbf{R}), \quad (7a)$$

$$\rho_i(\mathbf{r}) = [\varphi_i(\mathbf{r})]^2, \quad (7b)$$

$$h_X^{\text{HF,inter}}(\mathbf{r}, \mathbf{r} + \mathbf{R}) = h_X^{\text{HF}}(\mathbf{r}, \mathbf{r} + \mathbf{R}) - h_X^{\text{HF,intra}}(\mathbf{r}, \mathbf{r} + \mathbf{R}). \quad (7c)$$

While h_X^{HF} is independent of the choice of orbitals, its components $h_X^{\text{HF,inter}}$ and $h_X^{\text{HF,intra}}$ are not. This results from the fact that the electrons are indistinguishable, i.e. it is impossible to identify an individual electron within the electron system. Generally, the total exchange hole is dominated by the self-exchange part, however the relationship between intra- and inter-electronic exchange depends on the orbitals used for the description. The weight of the self-exchange part of the exchange

hole increases when localized rather than delocalized (canonical) orbitals are used.

For the case of a two-electron system, Eqs. (7a)–(7c) simplify to

$$h_X^{\text{HF, intra}}(\mathbf{r}, \mathbf{r} + \mathbf{R}) = h_X^{\text{HF}}(\mathbf{r}, \mathbf{r} + \mathbf{R}) = -\frac{1}{2}\rho(\mathbf{r}), \quad (8a)$$

$$h_X^{\text{HF, inter}}(\mathbf{r}, \mathbf{r} + \mathbf{R}) = 0, \quad (8b)$$

i.e., the exchange hole describes only the self-exchange of the electrons, and the corresponding exchange hole is independent of the position of the reference electron.

In LDA, exchange is described approximately by a model exchange hole, which has the form [8]

$$\begin{aligned} h_X^{\text{LDA}}(\mathbf{r}, \mathbf{r} + \mathbf{R}) &= -\frac{1}{2}\rho(\mathbf{r})J(2k_F R) \\ &= -\frac{1}{2}\rho(\mathbf{r})J(z), \end{aligned} \quad (9a)$$

$$J(z) = \frac{72}{z^6} [4 + z^2 - (4 - z^2) \cos z - 4z \sin z], \quad (9b)$$

where $k_F = [3\pi^2\rho(\mathbf{r})]^{1/3}$. The LDA model hole is spherically symmetric and becomes deeper and more compact the higher the density at the position of the reference electron is [8]. It is insensitive to all features of the electronic structure anywhere else than at \mathbf{r} . In general it cannot be represented by any distribution of the electron pairs; in particular the total electron pair density calculated with the LDA exchange hole may become negative.

The LDA exchange hole does not describe the self-exchange of an electron exactly. In SIC-LDA, this is remedied by replacing the LDA description of the self-exchange by an exact one:

$$\begin{aligned} h_X^{\text{SIC-LDA}}(\mathbf{r}, \mathbf{r} + \mathbf{R}) &= -\frac{1}{2}\rho(\mathbf{r}) \left[J(2k_F R) - 2 \sum_i \frac{\rho_i(\mathbf{r})}{\rho(\mathbf{r})} J(2k_{F,i} R) \right] \\ &\quad - 2 \sum_i \frac{\rho_i(\mathbf{r})}{\rho(\mathbf{r})} \rho_i(\mathbf{r} + \mathbf{R}), \end{aligned} \quad (10)$$

where $k_{F,i} = [6\pi^2\rho_i(\mathbf{r})]^{1/3}$. The inclusion of portions of HF exchange implies that the SIC-LDA exchange hole reflects details of the electronic structure, though to a lesser extent than with the HF exchange hole.

Generally, each presentation of the exchange hole (i.e., HF, LDA, or SIC-LDA) has to be calculated from the corresponding set of orbitals. In the following discussion, however, we will use HF orbitals in all cases to isolate those differences that are due to the different definitions of the exchange holes from effects due to differences in the one-particle density.

All calculations were carried out with Dunning's cc-pVTZ basis [18] at experimental geometries $\text{H}_2(^1\Sigma_g^+)$: 0.742 Å; $\text{F}_2(^1\Sigma_g^+)$: 1.412 Å [19]. For the SCF-SIC-DFT calculations, the generation of the difference densities, and the representation of the exchange holes, the program package COLLOGNE 2001 [20] was used.

3. How does the self-interaction error of DFT influence the exchange hole?

In Fig. 1, difference electron density distributions $\Delta\rho(\text{MP2}, \text{HF}) = \rho(\text{MP2}) - \rho(\text{HF})$ and $\Delta\rho(\text{S}, \text{HF}) = \rho(\text{S}) - \rho(\text{HF})$ are shown for the ground state of the H_2 and F_2 molecules at their equilibrium. The difference densities $\Delta\rho(\text{MP2}, \text{HF})$ (Figs. 1a and c) reveal how the HF density changes when electron correlation effects are included into the calculation. Electron pair correlation is introduced at the MP2 level of theory by double excitations, which transfer density out of the bond region toward the atoms (*left-right correlation*). Also, density is shifted from the inner region of the π -type electron lone pairs of F to the outer lone pair regions (*in-out correlation*, Fig. 1c) or, alternatively, from the σ -bonding region to the outer lone pair regions (*angular correlation*, Fig. 1c).

Although terms such as left-right, angular or in-out correlation were originally used to describe non-dynamic electron correlation effects introduced by a multi-configurational wave function (see, e.g. [21]), it is custom to use the same terms when describing dynamic electron correlation effects generated for example by a correlation corrected single determinant method such as MP2 [22] because difference electron density distributions show the same features [23].

The difference density $\Delta\rho(\text{S}, \text{HF})$ resembles that of $\Delta\rho(\text{MP2}, \text{HF})$ in so far as density is removed

from the bond to the nuclear regions (MP2, Figs. 1a and c; LDA, F_2 , Fig. 1d) and the non-bonding regions of the molecule (LDA, H_2 , Fig. 1b). Although the patterns of the calculated difference densities may look somewhat different (Figs. 1a and b), they suggest that LDA exchange similar as MP2 covers left–right electron correlation effects. The question is whether these correlation effects represent short-range (dynamic) electron correlation as in the case of MP2 or long-range (non-dynamic) electron correlation as anticipated in our previous work [11]. To answer this question the HF and the LDA exchange holes are compared in the following discussion.

In the case of H_2 , the HF exchange hole $h_X(\mathbf{r}, \mathbf{r} + \mathbf{R})$ is described by Eq. (8a), i.e. it adopts the form of one half of the negative of the σ_g^2 density and reflects the self-exchange of the two electrons [24]. Consequently, a change in the position of the reference electron, for example from the bond midpoint (position $\mathbf{r} = P1$) to one of the nuclei (position $\mathbf{r} = P2$), does not influence the form of the exchange hole, which is static and delocalized. Hence, HF intra-exchange (self-ex-

change) does not cover any Coulomb correlation effects. However, the HF exchange hole of H_2 bears features of the electronic structure of the molecule in the same way as the electron density $\rho(\mathbf{r})$ does.

The LDA exchange hole, in contrast, depends on the position of the reference electron (Fig. 2, positions P1 and P2) and is contrary to the HF exchange hole unstructured. It is always localized and centered at the position of the reference electron where one has to keep in mind that for reasons of comparison in Fig. 2 the same density was used. The exact and the LDA model exchange holes have in common that they are non-positive everywhere and that they are normalized to -1 . The lowest point of the LDA exchange hole for H_2 is equal to the negative electron density at this point, which means that at P1 the LDA hole is shallower and more diffuse while at P2 the hole becomes deeper and more contracted.

Since the same density is used for HF and LDA, the SIC-LDA exchange hole is identical to the HF exchange hole (Fig. 2). The SIE part of the LDA exchange hole is determined by subtracting the

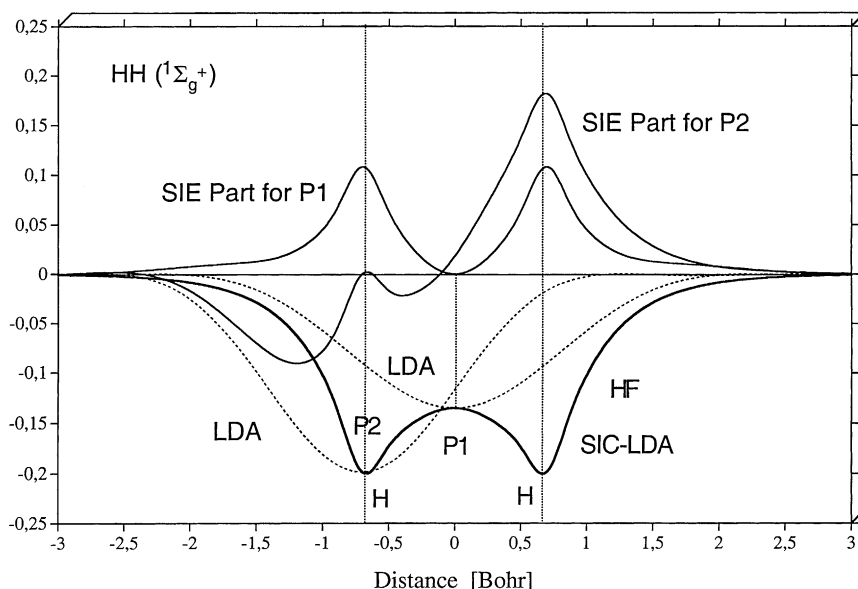


Fig. 2. Graphical representation of the exchange hole calculated for $H_2(^1\Sigma_g^+)$ along the bond axis at the HF, SIC-LDA (both bold lines), and LDA (S-only) levels of theory (dashed lines) for positions P1 and P2 of the reference electron. The SIE part of the LDA exchange hole is given by the lines in normal print. All calculations with a cc-pVTZ basis set at the experimental geometry.

SIC-LDA hole from the LDA hole. The SIE part can be both positive and negative (integrating to zero) and depends as the LDA exchange hole strongly on the position of the reference electron. If the latter is at P1, the SIE of LDA will raise the probability of finding the second electron close to the left or the right nucleus. If the reference electron is at P2, there will be a large probability of finding the second electron at the other nucleus, which is solely due to the SIE. It is noteworthy that at the position of the reference electron the SIE part must be exactly zero.

In the case of H_2 , the SIE takes over two important roles. (i) It compensates the delocalized structure of the SIC-DFT self-exchange hole to reproduce an unstructured, spherically symmetric localized DFT exchange hole. Therefore, it is structured and also related to wave function and electron density $\rho(\mathbf{r})$ where this relationship has to be seen in dependence of the position of the reference electron. At P1 the SIE part reflects the electronic structure close to the nuclei; at P2 it gives the situation at the other nucleus. (ii) The

SIE part of the LDA exchange hole mimics left–right electron correlation. This leads to a similar difference density pattern (Fig. 1b) as in the case of an MP2 density (Fig. 1a) but is in distinction from the latter case caused by long-range (non-dynamic) electron correlation effects.

Of course, H_2 represents an exceptional electron system possessing only self-exchange, which does not necessarily reflect the situation in a molecule with both intra- and inter-electronic exchange. Therefore, we will next investigate the situation in F_2 , which represents an 18 electron system (Figs. 3 and 4).

When the reference electron is at P1 (Fig. 3) the HF exchange hole adopts a symmetrical delocalized structure, which reminds of the (negative) electron densities of the $3\sigma_g$ bonding electron pair of F_2 . With regard to P1 this density should be symmetric and there are nodal planes at the positions of the nuclei. Since the reference electron is at a position where the orbital density of $3\sigma_g$ MO is relatively large, it is logical that this contribution dominates the shape of the HF exchange hole

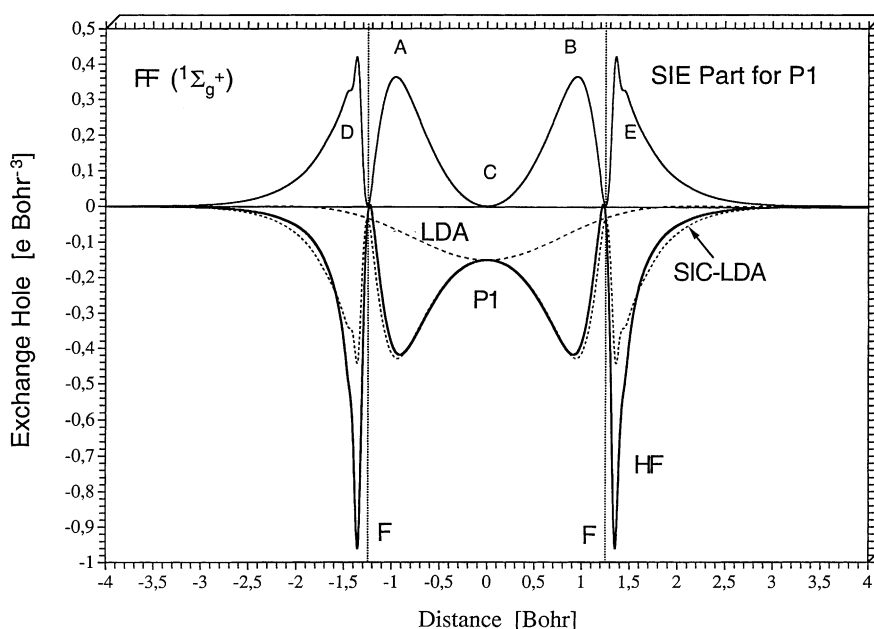


Fig. 3. Graphical representation of the exchange hole calculated for $F_2(^1\Sigma_g^+)$ along the bond axis at the HF (bold line), SIC-LDA (dotted line), and LDA (S-only) levels of theory (dashed line) for position P1 of the reference electron. The SIE part of the LDA exchange hole is given by the line in normal print. All calculations with a cc-pVTZ basis set at the experimental geometry.

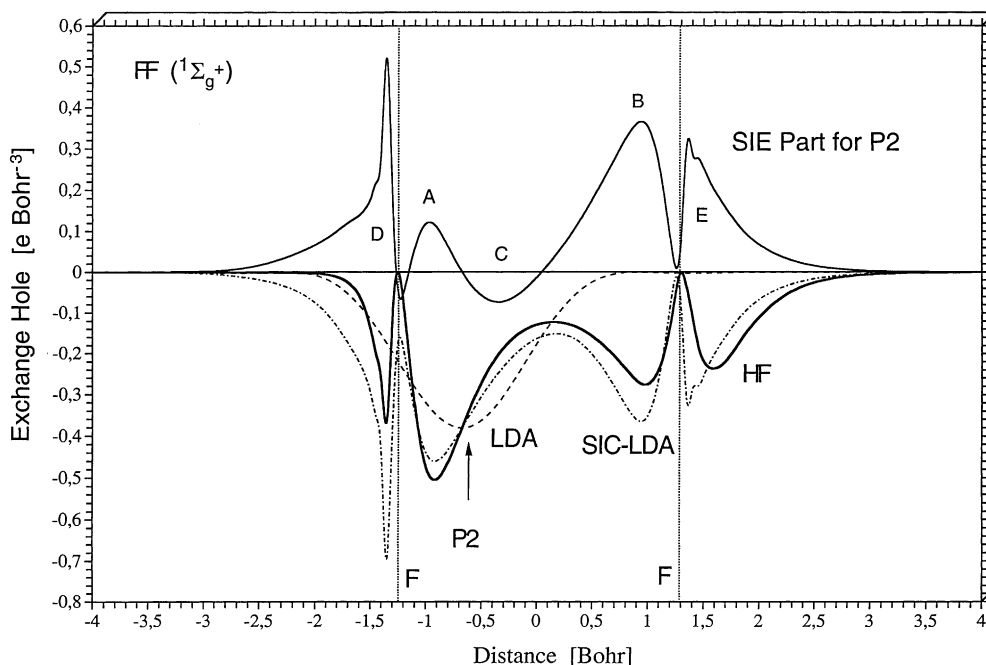


Fig. 4. Graphical representation of the exchange hole calculated for $F_2(^1\Sigma_g^+)$ along the bond axis at the HF (bold line), SIC-LDA (dotted line), and LDA (S-only) levels of theory (dashed line) for position P2 of the reference electron. The SIE part of the LDA exchange hole is given by the line in normal print. All calculations with a cc-pVTZ basis set at the experimental geometry.

(compare with Eq. (7a)). The influence of the other electrons on the form of the HF exchange hole is weighted by the square of the corresponding orbital density at P1 where one has to recall that localized orbitals (core, bonding and sp^3 -hybridized lone pair orbitals) are used to calculate the exchange hole. The core orbitals are completely localized in the core region and, therefore, their orbital density is close to zero at P1, i.e. they do not influence the structure of the HF exchange hole in the case of P1. There is a finite orbital density of the lone pair orbitals at P1. Accordingly, the exchange hole is significantly deepened in the lone pair regions (Fig. 3).

For each individual electron pair of F_2 , the self-exchange hole is static, i.e. it is not influenced by the position of the reference electron. For the core electron and the electron lone pairs the self-exchange hole is strongly or largely localized while for the bonding electron pair it is delocalized. The total HF self-exchange hole is no longer static but depends in its form on the position of the reference

electron. As for H_2 , the HF self-exchange hole integrates similarly as the total exchange hole to -1 , which implies that the inter-electronic part of the HF exchange hole must integrate to zero. Since for localized orbitals the self-exchange part is maximized, features of the total exchange hole can be discussed on the basis of the self-exchange.

As soon as the reference electron moves from P1 to P2 (Fig. 4), inter-electronic exchange should increase while intra-electronic exchange should remain constant as long as the reference electron stays in the bond region. The total exchange hole becomes deeper close to the reference electron in region A but shallower at the opposite site of the bond in region B. There is also a strong change in the lone pair region D: The (negative) intra-electronic exchange part of the lone pair increases because of the larger orbital density of the lone pair at P2, but at the same time there is also a (positive) increase of the inter-electronic exchange part because the probability of finding two electrons of the same spin at P2 and D increases when

they occupy different orbitals. In total, the HF exchange hole becomes less deep at the position D compared to the situation with the reference electron at P1. At position E, there is no longer a lone pair contribution to intra-electronic exchange because the orbital density of the corresponding lone pairs is too small at P2. However, there is again a positive inter-electronic contribution leading to a broadening and flattening of the total HF exchange hole at E.

The SIC-LDA exchange hole resembles the HF exchange hole in the vicinity of P2 (regions A and C; Fig. 4) but differs in other regions. Again, this is due to the inter-electronic exchange that is handled differently at HF and LDA. The self-exchange part of the SIC-LDA hole adjusts to the HF self-exchange part, however the inter-electronic part takes the spherical symmetrical form enforced by LDA exchange. The LDA exchange hole (Fig. 4) is centered at P2 and approaches zero in regions D, B, and E. The same holds for the inter-electronic LDA exchange, which implies that in these regions the SIC-LDA hole is dominated by the intra-electronic part. Hence it becomes more symmetrical in the bond region, deeper in region D and less deep in region E.

This can be more clearly seen if the reference electron is at P1 (Fig. 3). Then, HF and SIC-LDA exchange hole are literally identical in the bond region but differ due to the (positive) inter-electronic contributions in the lone pair regions D and E. The structure of the SIC-LDA hole reflects again the electronic structure of the molecule as does the SIE part of the LDA hole. The latter becomes almost the mirror image of the SIC-LDA hole and reveals that the probability of finding a second electron will increase in regions A and B as well as D and E if the reference electron is at P1.

In the case that the reference electron is at P2, the SIE leads to a significantly increased probability of finding the other electron at B in the bond region or at D and E in the lone pair regions. Clearly, the SIE part mimics long-range non-dynamic electron correlation. This explains the difference electron distribution $\Delta\rho(S, \text{HF}) = \rho(S) - \rho(\text{HF})$ shown in Fig. 1d.

We draw the following conclusions from the present study.

1. HF exchange is not always, as often anticipated, delocalized. If the reference electron is at the position of the nucleus, both the HF, LDA, and SIC-LDA exchange holes are strongly localized because in this case the dominant contributions to the exchange hole result from the core orbitals. The localized or delocalized character of the HF exchange hole solely depends on the position of the reference electron and the electronic structure of the molecule.
2. It is useful to partition HF exchange into intra- and inter-electronic parts. Although this partitioning depends on the type of orbitals used for the representation, it is reasonable to define these quantities with the help of localized orbitals because the latter maximize the intra-electronic part of the HF exchange energy. For one electron pair (example H_2), the intra-electronic (self-exchange) part is static, i.e. it does not depend on the position of the reference electron.
3. The SIC-LDA exchange hole is influenced by two factors, namely (a) the correct self-exchange part of HF (where normally one has to consider the difference in HF and DFT densities which was suppressed in this work) and (b) a spherically symmetric inter-electronic LDA exchange part, which is responsible for the deviations between HF and SIC-LDA exchange holes.
4. Both HF and SIC-LDA hole reflect the electronic structure of the molecule in the larger vicinity of the reference electron. Since the structure of the LDA exchange hole is independent of the electronic structure of the molecule (the minimum of the hole gives only the negative of the electron density at this point), the difference between LDA and SIC-LDA exchange holes, i.e. the SIE part, must reflect electronic structure features.
5. The spatial variation in the SIE part of the LDA hole is such that a second electron is removed from the reference electron by a relatively large distance, which amounts to half a bond distance or even more. Hence, the SIE part mimics long-range non-dynamic electron correlation.

By carrying out the analysis described in this work the amount of long-range electron correlation covered by a given exchange functional can be quantified. Work is in progress to apply a similar analysis in the case of GGA functionals.

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