

Gradient corrections to the Hartree-Fock-Slater exchange and their influence on bond energy calculations

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Summary. Density functional approximations based on a local representation of the exchange energy tend to over-estimate bond energies. We show that the tendency is due to the incorrect form of the Fermi hole correlation function adopted by these methods. This function is adequate at the maxima of the radial density in isolated atoms, at the corresponding maxima of atoms in molecules, and at the saddle points of the molecular density in the bonding regions. However, the Fermi hole correlation function yields too low exchange energy contributions in absolute terms from the tails of the core shells and the valence density. On bond formation electron density is transferred from the tails of the atomic core shells to the density maximum of the valence shell. At the same time, parts of the atomic valence tails are transformed into the bonding region with a saddle point. In both cases the contributions from the tail regions to the exchange energy are under-estimated in the local approximation, with the result that the calculated bond energies are too large. Similar considerations can be used to explain why local exchange density functional methods under-estimate ionization potentials.

The addition of non-local gradient correction terms to the local exchange functionals greatly improves calculated bond energies and ionization potentials by rectifying the qualitatively incorrect behaviour of the local Fermi hole correlation function in the tails of the core shells and the valence density. A detailed graphic analysis is provided of the contributions from non-local corrections to the calculated bond energies.

Key words: Hartree-Fock-Slater exchange – Bond energy calculations – Gradient corrections

1. Introduction

The Hartree-Fock-Slater (HFS) method is an exchange-only theory based on the local density approximation. The inadequacy of the local approximation for atoms, including its tendency to under-estimate atomic exchange energies, has been thoroughly investigated [1, 2]. Another shortcoming of the HFS-method is its tendency to over-estimate molecular dissociation energies, in particular for

metal-ligand and metal-metal bonds. In a series of pioneering papers, Becke [3–5], Langreth and Mehl [6], Perdew [7a,b] and others [7c–e] have eliminated many of the shortcomings of the local approach by introducing correction terms based on electron density gradients. The non-local correction terms greatly improve the calculation of atomic exchange energies [1, 3–7] and afford in addition bonding energies far superior to the HFS results [3–5, 8].

In a previous study [1] we have provided a detailed analysis of how non-local gradient corrections improve the calculated atomic exchange energies. Our analysis was based on the Fermi hole correlation functions [9] and we were able to demonstrate how non-local gradient terms rectify the qualitatively incorrect behaviour of the HFS Fermi hole correlation functions in the tails of the core-shells and the valence density [1].

The objective of the present study is to investigate how non-local gradient corrections influence calculations on bond energies. Our analysis will again be tied to the properties of the Fermi hole correlation function. We shall establish that the qualitatively incorrect behaviour of the HFS Fermi hole correlation functions in the tails of the core-shells and the valence density also are responsible for the over-estimation of bond energies in the local approximation. We shall further demonstrate how the non-local corrections improve the calculated bond energies by rectifying the qualitatively incorrect behaviour of the HFS Fermi hole correlation functions. Our analysis will finally be extended to the calculation of ionization potentials.

2. The exchange energy and the Fermi hole correlation function

We shall begin by introducing a few concepts of importance for a discussion of the electronic exchange. The exchange energy is defined as:

$$E_x^{\gamma\gamma} = -\frac{1}{2} \int \frac{\rho_1^\gamma(\vec{r}_1) \rho_x^{\gamma\gamma}(\vec{r}_1, \vec{r}_2)}{r_{12}} d\vec{r}_2; \quad \gamma = \alpha, \beta \quad (1)$$

where $\rho_1^\gamma(\vec{r}_1)$ is the one electron density and $\rho_x^{\gamma\gamma}(\vec{r}_1, \vec{r}_2)$ the Fermi hole correlation function. $E_x^{\gamma\gamma}$ is completely determined by the spherical average of the hole correlation function [9]:

$$\bar{\rho}_x^{\gamma\gamma}(\vec{r}_1, s) = \frac{1}{4\pi} \int \rho_x^{\gamma\gamma}(\vec{r}_1, \vec{r}_1 + \vec{s}) \delta\Omega_s, \quad (2)$$

with $\vec{r}_1 + \vec{s} = \vec{r}_2$ and $s \equiv r_{12} = |\vec{s}|$. Thus [9]:

$$E_x^{\gamma\gamma} = -\frac{4\pi}{2} \int \frac{\rho_1^\gamma(\vec{r}_1) \bar{\rho}_x^{\gamma\gamma}(\vec{r}_1, s)}{s} d\vec{r}_1 s^2 ds. \quad (3)$$

It is important to note that the Fermi hole correlation function is normalized to unity. Eq. (3) can be recast as:

$$E_x^{\gamma\gamma} = \int \varepsilon_x^{\gamma\gamma}(\vec{r}_1) d\vec{r}_1 = \frac{1}{2} \int \rho_1^\gamma(\vec{r}_1) V_x^{\gamma\gamma}(\vec{r}_1) d\vec{r}_1, \quad (4a)$$

with

$$V_x^{\gamma\gamma}(\vec{r}_1) = -4\pi \int \frac{\bar{\rho}_x^{\gamma\gamma}(\vec{r}_1, s)}{s} s^2 ds. \quad (4b)$$

The term $V_x^{\text{FH}}(\vec{r}_1)$ represents the Coulomb potential due to the spherically averaged Fermi-hole correlation function $\bar{q}_{X\alpha}^{\text{FH}}(\vec{r}_1, s)$. We shall refer to $V_x^{\text{FH}}(\vec{r}_1)$ and $\varepsilon_x^{\text{FH}}(\vec{r}_1)$ as the exchange potential and the exchange energy density, respectively.

The hole function in the HFS method is based on the approximate expression:

$$\bar{q}_x^{\text{FH}}(\vec{r}_1, s) \cong \bar{q}_{X\alpha}^{\text{FH}}(\vec{r}_1, s) = 9 \cdot q_1^{\text{FH}}(\vec{r}_1) \frac{[\sin(k_f^{\text{FH}}s) - (k_f^{\text{FH}}s) \cos(k_f^{\text{FH}}s)]^2}{(k_f^{\text{FH}}s)^6}, \quad (5)$$

where $k_f^{\text{FH}} = [6\pi^2 q_1^{\text{FH}}(\vec{r}_1)]^{1/3}$. It is characteristic for the approximate hole function, $\bar{q}_{X\alpha}^{\text{FH}}(\vec{r}_1, s)$, that it has its principal maximum at $s = 0$ irrespective of the position of \vec{r}_1 , see Fig. 1a. The exchange potential in the HFS-method is given by:

$$V_{X\alpha}^{\text{FH}}(\vec{r}_1) = -\frac{9}{2} \alpha_x \cdot \left(\frac{3}{4\pi}\right)^{1/3} [q_1^{\text{FH}}(\vec{r}_1)]^{1/3}, \quad (6)$$

with $\alpha_x = 2/3$, as it follows from Eq. (5). In some applications, the term α_x is used as an adjustable parameter, with the optimal value of $\alpha_x = 0.7$.

The local description of exchange has a number of deficiencies as discussed in more details in a previous study on atomic systems [1]. The deficiencies are related to the fact that the approximate hole-function $\bar{q}_{X\alpha}^{\text{FH}}(\vec{r}_1, s)$ has its maximum at $s = 0$ for *all* positions of \vec{r}_1 [1]. This feature is manifestly incorrect when \vec{r}_1 is in the tails of either the core shells or the valence shell [1]. In those regions the exact function has its maximum at $s > 0$, see Fig. 1b. It follows further from Fig. 1b that the function $\bar{q}_{X\alpha}^{\text{FH}}\alpha(\vec{r}_1, s)$ is too diffuse in the tail regions and it can readily be shown [1] that the corresponding potential, $V_{X\alpha}^{\text{FH}}(\vec{r}_1)$, is too weak. The shape of $\bar{q}_{X\alpha}^{\text{FH}}\alpha(\vec{r}_1, s)$ is much more adequate at the maximum of the radial density $r_1^2 \rho_1^{\text{FH}}$ in any atomic shell. Here, the exact function has also its maximum as $s = 0$, Fig. 1a. At such maxima $V_{X\alpha}^{\text{FH}}(\vec{r}_1)$ resembles closely the exact exchange potential for atoms.

Simple non-local corrections to the HFS exchange have been developed in the past years [3–6] in order to rectify some of the deficiencies of the local theories delineated above. The potential in the non-local theories is given by [3–6]:

$$V_{x\text{NL}}^{\text{NL}}(\vec{r}_1) = V_{X\alpha}^{\text{FH}}(\vec{r}_1) + V_{\text{GC}}^{\text{NL}}(\vec{r}_1), \quad (7)$$

where the non-local correction to the exchange potential, $V_{\text{GC}}^{\text{NL}}(\vec{r}_1)$, can be expressed as:

$$V_{\text{GC}}^{\text{NL}}(\vec{r}_1) = \beta_x \int (\chi^{\text{NL}})^2 [q_1^{\text{FH}}(\vec{r}_1)]^{1/3} G[\chi^{\text{NL}}] \cdot d\vec{r}_1, \quad (8a)$$

where

$$\chi^{\text{NL}} = \frac{|\nabla q_1^{\text{FH}}(\vec{r}_1)|}{[q_1^{\text{FH}}(\vec{r}_1)]^{4/3}}, \quad (8b)$$

and β_x is a numerical parameter.

In general, the term $G[\chi^{\text{NL}}]$ in Eq. (8a) has the properties of a cut-off factor which vanishes asymptotically for large values of χ^{NL} . A particularly appropriate form for $V_{\text{GC}}^{\text{NL}}(\vec{r}_1)$ has recently been developed by Becke [5a]. Becke's correction has the property that the corresponding potential of Eq. (7) has the correct asymptotic limit of $-1/r_1$ for atoms. This represents an improvement over the simple local potential $V_{X\alpha}^{\text{FH}}(\vec{r}_1)$ with its unphysical exponential asymptotic limit.

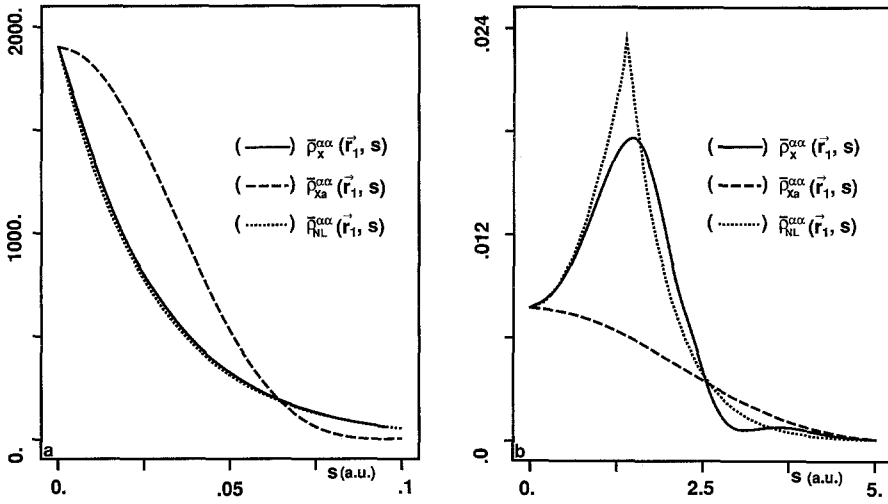


Fig. 1a,b. Ar atom: the spherically averaged Fermi hole correlation functions $\bar{q}_x^{\alpha\alpha}(\vec{r}_1, s)$ (exact Hartree-Fock), $\bar{q}_{X\alpha}^{\alpha\alpha}(\vec{r}_1, s)$, and $\bar{q}_{NL}^{\alpha\alpha}(\vec{r}_1, s)$. a At the nucleus (maximum of the K shell). b In the tail of the valence shell ($r_1 = 2.5$ a.u.)

We shall adopt the expression given by Becke [5a] throughout the following discussion.

A comparison between the exact Fermi hole correlation function, the local expression of Eq. (9), and the non-local Fermi hole correlation function is shown in Fig. 1. The non-local Fermi hole correlation function is represented by the model expression of Tschinke and Ziegler [1]. The non-local hole correlation function differs only slightly from $\bar{q}_{X\alpha}^{\alpha\alpha}(\vec{r}_1, s)$ at the density maxima, where the exact function $\bar{q}_x^{\alpha\alpha}(\vec{r}_1, s)$ also has its maximum at $s = 0$. However, it differs significantly from $\bar{q}_{X\alpha}^{\alpha\alpha}(\vec{r}_1, s)$ in the tail regions where it takes on a maximum at $s > 0$ in analogy with the exact function $\bar{q}_x^{\alpha\alpha}(\vec{r}_1, s)$, Fig. 1b. The non-local corrections to the potential is depicted in Fig. 2. Figure 2a exhibits the gradient correction $V_{GC}^{\alpha\alpha}(\vec{r}_1)$ for the N-atom. The correction has a local minimum at $r_1 = 0$, increases at the edge of the K shell and then decreases again at the density maximum of the valence shell. Finally the correction increases at the onset of the valence density tail. Not surprisingly, the gradient correction for the N_2 molecule reveals a similar shell structure and analogous asymptotic behaviour, see Fig. 2b. However, some differences can be observed, most notably in the bond region. We shall discuss their implications for the calculation of bond energies in the next section.

3. Non-local corrections to the bond energy

We display in Table 1 the dissociation energies of several diatomics as well as the dimerization energies for $CH_{(n)}$ ($n = 1, 2, 3$). The computational methods include the HFS-, LDA- [10], and LDA/NL- [3] schemes. The LDA (Local Density Approximation) method adopts the HFS energy expression augmented by accurate local correlation corrections [11] for electrons of opposite spins. The LDA/NL contains further the gradient correction to the exchange given in Eq. (7).

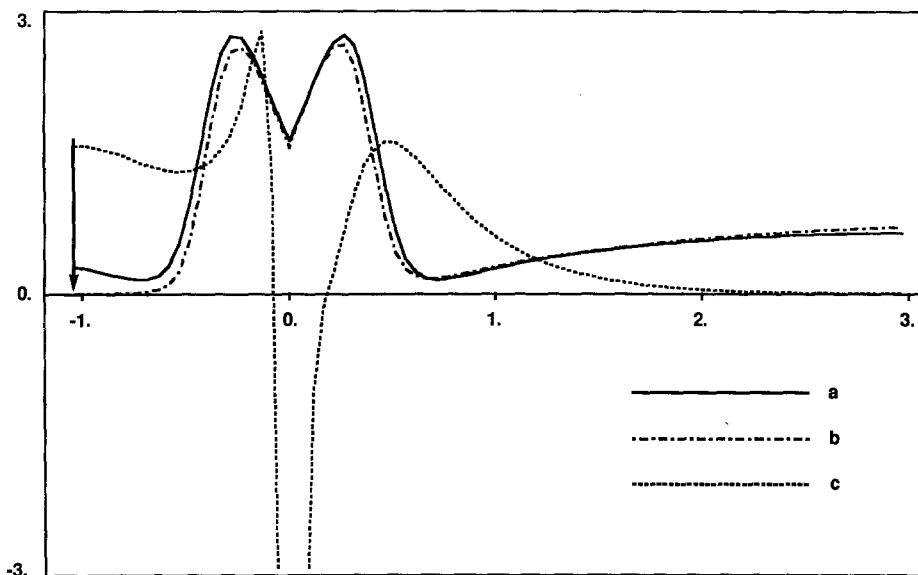


Fig. 2. The gradient correction to the exchange potential for the N atom. The plot gives the average $-\left[\bar{q}_1^x \cdot V_{GC}^{xx} + \bar{q}_1^y \cdot V_{GC}^{yy}\right]/(q_1^x + q_1^y)$. **b** The gradient correction $-V_{GC}^{xx} = -V_{GC}^{yy}$ of the N_2 molecule along the bond axis. **c** Deformation density for the N_2 molecule; the mid-bond region is located at -1.035 a.u.

The bond energies calculated by the HFS method are seen to be too large in most cases. Further, as opposite spin correlation is included (LDA-method) the calculated bond energies are always too large compared to experiment, with the exception of the Li_2 molecule (*vide infra*). Gradient corrections [5a] to the HFS exchange (LDA/NL) bring the calculated values [4, 5b, 7] to within a few tenth of eV from experiment. We shall now demonstrate that there is a direct connection between the qualitatively incorrect behaviour of $\bar{q}_{X_2}^{yy}(\vec{r}_1, s)$ and the tendency of the local method to over-estimate bond energies. We shall further illustrate how the deficiencies are rectified by the non-local corrections.

Consider as an example the N_2 molecule for which the non-local correction is essential to bring the calculated bond energy in-line with experiment, Table 1. The contribution from the gradient correction to the bond energy is given by:

$$E_{NL}^{BOND} - E_{HFS}^{BOND} = \Delta E_{xNL} - \Delta E_{xHFS} \\ = \frac{1}{2} \int d\vec{r}_1 \sum_{\gamma=\alpha}^{\beta} \left[\sum_A q_{1,A}^{\gamma}(\vec{r}_1) V_{GC,A}^{\gamma}(\vec{r}_1) - q_{1,M}^{\gamma}(\vec{r}_1) V_{GC,M}^{\gamma}(\vec{r}_1) \right], \quad (9)$$

where the index A indicates a sum over atoms and M represents the molecule. The argument of the integral in Eq. (9) is depicted in Fig. 3 for the N_2 molecule. It is predominantly negative, consistently with the fact that gradient corrections will reduce the bond energy, Table 1. We note two significant contributions from the gradient correction. One is found close to each N nuclei and the other in the mid-bond region. We shall now in turn discuss the contribution from each region.

Table 1. Dissociation energies (eV)

	HFS ^a	LDA ^a	LDA/NL ^{a,b}	Exp. ^c
H ₂	3.5	4.9	5.1 (+0.2)	4.75
Li ₂	0.3	1.0	0.9 (-0.1)	1.14
B ₂	3.5	3.9	2.8 (-1.1)	3.0
C ₂	6.2	7.3	5.6 (-1.7)	6.36
N ₂	0.09	11.2	9.81 (-1.4)	9.91
O ₂	6.85	7.35	5.26 (-2.1)	5.21
F ₂	3.18	3.34	1.81 (-1.5)	1.66
Na ₂	—	0.9	0.7 (-0.2)	0.7
Al ₂	—	2.0	1.3 (-0.7)	1.6
Si ₂	—	4.0	3.1 (-0.9)	3.2
P ₂	—	6.2	5.0 (-1.2)	5.1
S ₂	—	5.9	4.5 (-1.4)	4.4
Cl ₂	—	3.6	2.3 (-1.3)	2.5
CO	11.84	12.68	10.81(-1.9)	11.08
NO	7.03	8.36	6.66 (-1.7)	6.62
2CH → C ₂ H ₂ ^d	11.20	11.57	9.43 (-2.2)	10.26 ^e
2CH ₂ → C ₂ H ₄ ^d	7.24	8.46	7.02 (-1.5)	7.07 ^e
2CH ₂ → C ₂ H ₆ ^d	4.32	4.81	3.40 (-1.4)	3.82 ^e

^a All calculated values from Becke AD [5], except N₂, F₂, CO, NO, and CH_(n) dimerization energies, from Tschinke V and Ziegler T [7]. A value of $\alpha_x = 2/3$ was used for all the results in the Table, except for the HFS calculations from Ref. [7], for which a value of $\alpha_x = .7$ was adopted

^b In brackets, gradient correction to the bond energy. Beck used the non-local functional of Ref. [5a], Tschinke and Ziegler the non-local functional of Ref. [4]

^c Huber KP, Herzberg G (1979) Molecular spectra and molecular structure IV: constant of diatomic molecules. Van Nostrand Reinhold, New York

^d Dimerization energy

^e (a) Darwent B deB (1970) Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.A.) 31

(b) "JANAF Tables of Thermochemical Data", Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.) 37 (1971)

(a) *The atomic core region.* Figure 2c displays the change in electron density on bond formation. It follows that density is removed from the core region. This removal is associated with a promotion of charge from the $2s$ - to the $2p$ -orbital as the bond is formed. Since it has a non-zero value at the nucleus, the $2s$ -orbital penetrates into the core region to a greater extent than the $2p$ -orbital. Thus, when the promotion to the $2p$ -orbital takes place, electron density is shifted from the core region to the valence region of the atom. The core region is dominated by the tail of the $1s$ -orbital, while the valence region is dominated by the maximum of the radial density in the L -shell. The HFS approximation under-estimates, as already mentioned, the contribution to the exchange energy from the core tail whereas it is adequate at the maxima of the radial density. The promotion energy, in which density is shifted from the core tail to the valence maxima, is as a consequence under-estimated in the HFS theory. This error will largely contribute to the general over-binding which is so characteristic for the local methods, Table 1. The poor representation of ns to np promotion energies in the local approximation is illustrated in Fig. 4 for the N, O, and F atoms.

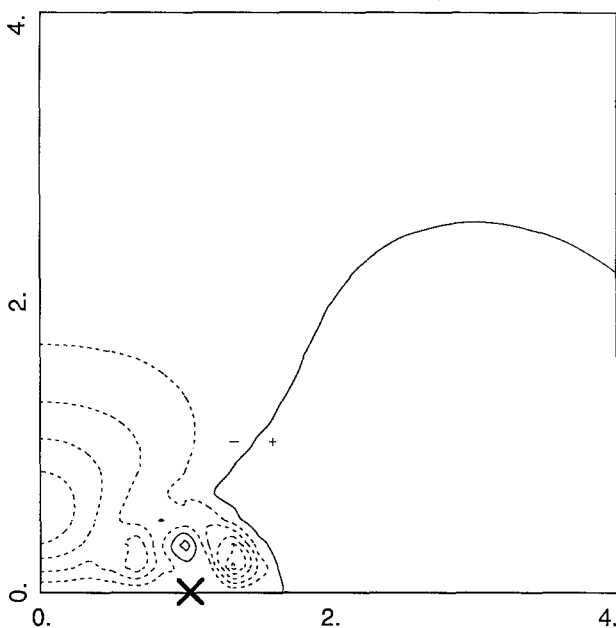


Fig. 3. The gradient correction contribution to the bond energy of the N_2 molecule, see Eq. (9). Only one of the 4 symmetry equivalent quadrants in the xz plane is shown. The atom on the z -axis (horizontal axis in plot) is marked by a cross. All values are multiplied by the factor r equal to the radial distance from the bond axis. *Solid lines:* positive and zero values; *dotted lines:* negative values. Contour line increment is .001 a.u.

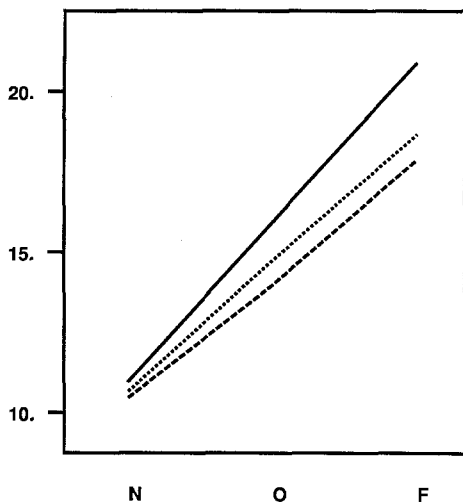


Fig. 4. $2s \rightarrow 2p$ promotion energies for the N, O, and F atoms, in eV. (—): experimental values; (---): HFS + gradient correction; (---): HFS method

The gradient corrected theory of Eq. (7) provides on the other hand an adequate estimate of the exchange energy contribution from the core tail as well as the radial density maximum. The calculated non-local bond energies (LDA/NL) in Table 1 are as a consequence better in line with experiment. It is further illustrated in Fig. 4 that the non-local correction improves the calculated ns to np promotion energies. Gunnarsson and Jones have previously suggested a connection between the inability of the local approximations to calculate promotion energies accurately and their tendency to over-estimate bond energies [12]. We shall now discuss another error source located in the bonding region.

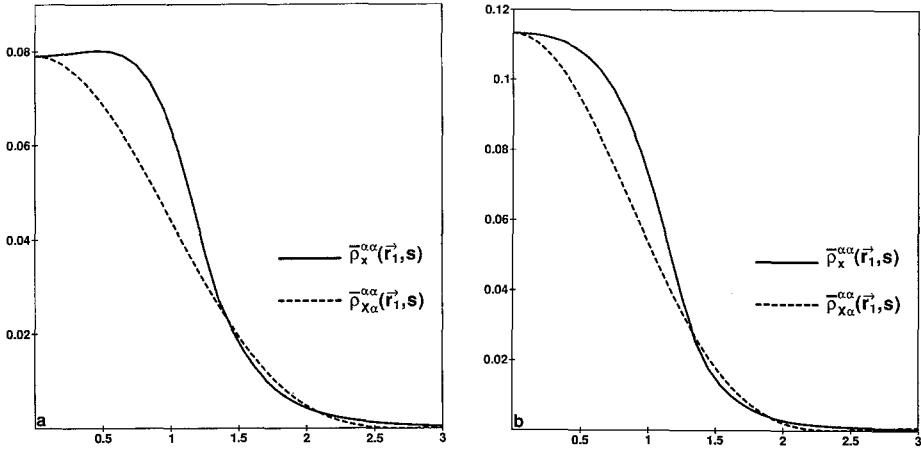


Fig. 5a,b. The spherically averaged hole correlation functions $\bar{\rho}_x^{\alpha\alpha}(\vec{r}_1, s)$ and $\bar{V}_{X_\alpha}^{\alpha\alpha}(\vec{r}_1, s)$; **a** for the N-atom at a distance $r_1 = 1.44$ from the nucleus; **b** for the N₂ molecule at the same distance from the nucleus as in **a**), at 1 a.u. on the line bisecting the bond axis

(b) *The molecular bonding region.* Parts of the atomic valence tails are gradually transformed into the bonding region as the two N atoms approach each other. For a reference electron positioned in the region of transformation, the spherically averaged Fermi hole correlation function $\bar{q}_x^{\gamma\gamma}$ changes its shape from that typical of an atomic valence tail, with its maximum at $s > 0$, Fig. 5a, to the shape characteristic of a region dominated by density accumulation, with its maximum as $s = 0$, Fig. 5b. The HFS method represents the tail region poorly with an inappropriate hole function $\bar{q}_{X_\alpha}^{\gamma\gamma}$, see Fig. 5b, and a potential $V_{X_\alpha}^{\gamma\gamma}(\vec{r}_1)$ that is much too weak. The bonding region generated after the formation of the molecule is on the other hand described more adequately by the HFS method, both with respect to the hole function $\bar{q}_{X_\alpha}^{\gamma\gamma}$, see Fig. 5a, and the potential $V_{X_\alpha}^{\gamma\gamma}(\vec{r}_1)$. The imbalance between the HFS-description of the valence tail present *before* the bond formation, from which the contribution to the total atomic exchange energy is too small in absolute terms, and the bond region present *after* forming the molecule, from which the contribution to the total molecular exchange energy is adequate, will further enhance the tendency of the HFS method to over-estimate bond energies.

The non-local theory rectifies this imbalance by introducing a stabilizing correction, $V_{GC}^{\gamma\gamma}(\vec{r}_1)$, to the potential in the tail of the atomic valence density, Fig. 2a. $V_{GC}^{\gamma\gamma}(\vec{r}_1)$ is instead negligible in the molecular bonding region (Fig. 2b). The bond energies calculated by the non-local corrections are as a result reduced considerably, Table 1.

4. Extensions to different and larger molecules

The discussion presented for the N₂ molecule can be applied as well to other diatomics. The contributions from the gradient correction to the bonding energy is depicted for the B₂, C₂, O₂, and F₂ molecules in Fig. 6. The general behaviour of the correction is similar to the case of the N₂ molecule. A destabilization from the $2s \rightarrow 2p$ promotion is observed around each nucleus. Also, destabilizing contributions are observed in the mid-bond region. In all cases the gradient

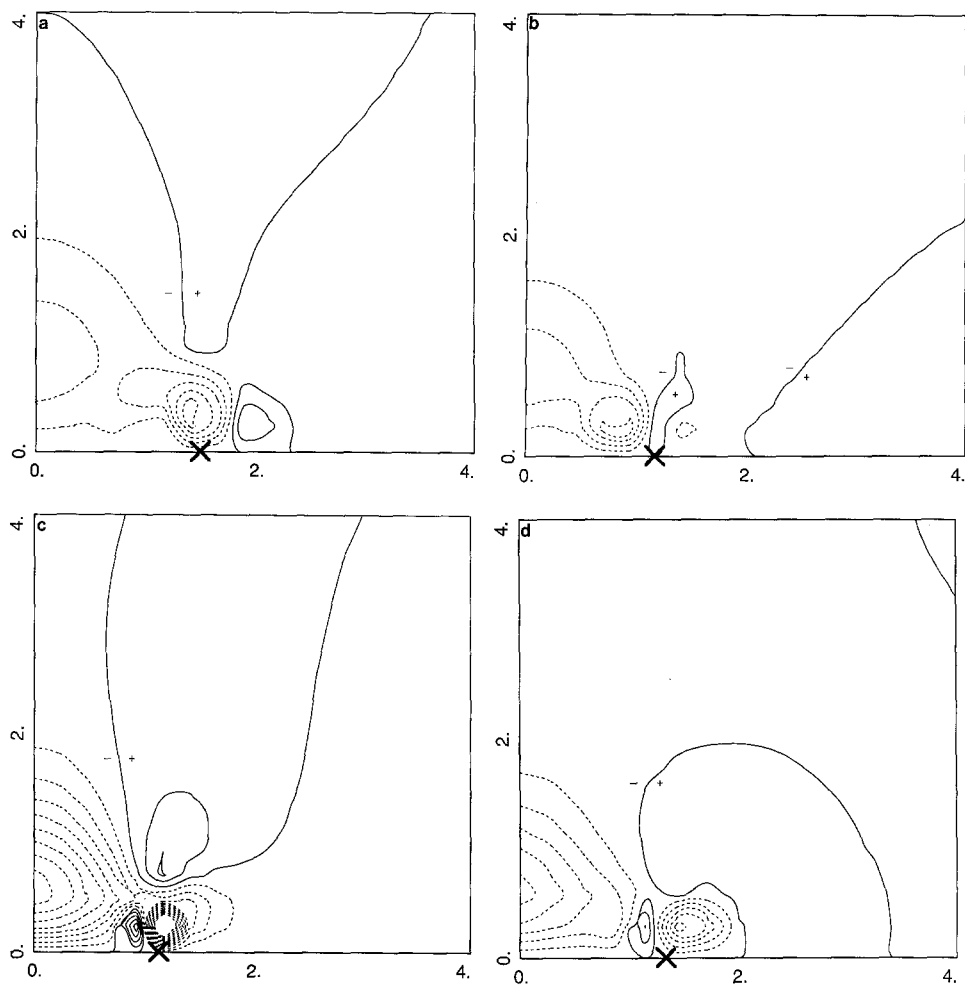


Fig. 6a–c. Plots of the gradient correction to the bond energy for B_2 , C_2 , O_2 , and F_2 molecules. Coordinate specifications as in Fig. 3. All values are multiplied by the factor r equal to the radial distance from the bond axis. *Solid lines*: positive and zero values; *dotted lines*: negative values. **a** B_2 molecule, **b** C_2 molecule, **c** O_2 molecule, **d** F_2 molecule. Contour line increment is 0.001 a.u.

correction is essential to ensure good agreement of the calculated bond energies with experiment, see Table 1.

The gradient corrections to the bond energy of the Li_2 and the H_2 molecules are depicted in Fig. 7. The correction around each nucleus is minimal since the promotion energy contribution is either totally absent (H_2) or rather small (Li_2). Further, hydrogen and lithium have rather diffuse valence orbitals [13] compared to the bond distances in H_2 and Li_2 , respectively. At rather large distances from the nuclei where the gradient correction is important, the density and its gradient are of similar magnitude for the molecule and the isolated atoms. Thus, the expression of Eq. (9) is small everywhere at large distances from the nuclei.

The gradient corrections to the bond energies of second row diatomics follow closely their first row counterparts. Thus Na_2 has a small correction by analogy

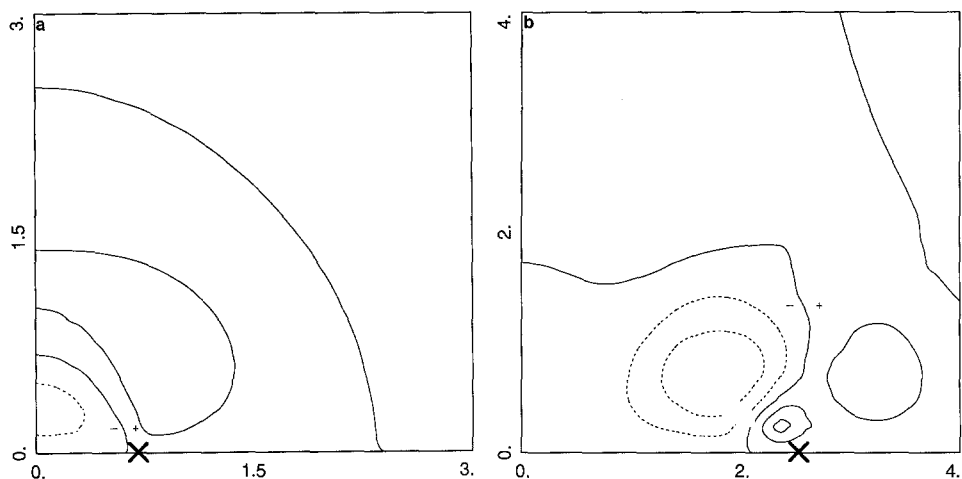


Fig. 7. Plots of the gradient correction to the bond energy for the H_2 and Li_2 molecules. Coordinate specifications as in Fig. 3. All values are multiplied by the factor r equal to the radial distance from the bond axis. *Solid lines*: positive and zero values; *dotted lines*: negative values. **a** H_2 molecule; Contour line increment is 0.0005 a.u. **b** Li_2 molecule; contour line increment is 0.001 a.u.

with the Li_2 molecule, while the diatomics from Al_2 to Cl_2 are characterized by larger corrections.

Bond formation between molecular fragments can be analyzed in the same way as bond formation between atoms. Consider for instance the dimerization of CH , CH_2 , and CH_3 to form ethyne, ethene, and ethane. Table 1. By isolobal analogy, the first bond is related to N_2 , the second to C_2 , whereas the last is related to F_2 . We find again that the gradient correction significantly improves the calculated bond energies.

The tendency of the HFS and LDA methods to over-bind molecular fragments is particularly evident for transition metal complexes. Recent work [14] has shown that the gradient correction is able to bring the calculated bond energies to within 10–20 kJ mol^{-1} of the experimental values. Several such examples are reproduced in Table 2.

Table 2. Bond energies^a (kJ mol^{-1})

	HFS	LDA	LDA/NL	Exp.
$\text{HMn}(\text{CO})_5^b$	—	—	225	213
$\text{CH}_3\text{Mn}(\text{CO})_5^b$	—	—	153	153
$\text{HCo}(\text{CO})_4^b$	—	—	230	238
$\text{Cr}(\text{CO})_6^c$	272	276	147	162
$\text{Mo}(\text{CO})_6^c$	226	226	119	126
$\text{W}(\text{CO})_6^c$	238	247	142	166
$\text{Fe}(\text{CO})_5^c$	263	263	185	176
$\text{Ni}(\text{CO})_4^c$	188	192	106	104

^a Ziegler et al. [14] and references therein. $\alpha_x = 2/3$, except for the HFS results ($\alpha_x = .7$). Non-local functional of Ref. [4]

^b M-H or M- CH_3 dissociation energy

^c First metal-carbonyl dissociation energy

The Hartree–Fock method contains by definition the exact Fermi hole correlation function. The non-local corrections are based on a Taylor expansion of the exact Fermi hole correlation function $\bar{q}_x^{xy}(\mathbf{r}_1, s)$ about $s = 0$ [1, 3]. Thus, they reproduce the behaviour of the HF-hole function for *small values* of the inter-electronic distance, s . For isolated *atoms*, this is sufficient to align the values of the non-local expression to the Hartree–Fock values, as already shown in Fig. 1.

For this reason, it might seem somewhat puzzling that the “exact” HF exchange theory in many instances fares poorly *in molecules* compared to HFS and its non-local extension. Thus, bond energies calculated by the HF method deviate [15b,f] by as much as 5 eV for some of the molecules displayed in Table 1. The deficiencies of the HF method have been studied extensively for molecules [15]. The molecular HF-hole function, $\bar{q}_{\text{HF}}^{xy}(\mathbf{r}_1, s)$, is very diffuse [15c–d] as a function of the inter-electronic distance, s , for certain positions of \mathbf{r}_1 , in particular in the limit of bond dissociation. This deficiency is often referred to as the near-degeneracy error. It can be rectified by a limited configuration interaction treatment [15a,e]. The hole functions of the HFS method and its non-local extensions do not have the same inappropriate shape for *large values* of s [15c–d] as $\bar{q}_{\text{HF}}^{xy}(\mathbf{r}_1, s)$ does. As a consequence they do not suffer from the near-degeneracy error introduced by the HF-method. A more detailed discussion of these points has been given elsewhere [15c–d].

5. Ionization energies

In Table 3, we compare calculated first and second ionization energies for a number of molecules with experimental values. The HFS-method provides too small ionization energies, whereas the larger LDA values are more in line with experiment. However, as shown in Table 3, the correlation correction to the HFS-method, while of the right sign, is not large enough to align LDA ionization energies with experiment, leaving some room – and need – for further improvement of the HFS-method.

In Table 3 we present ionization energies given by the LDA method with the addition of gradient corrections, under the header LDA/NL. It follows from Table 3 that the non-local correction in most cases increases the calculated ionization energies thus bringing the LDA/NL values closer in line with experiment than the LDA ionization energies.

It is also evident that the LDA/NL ionization energies tend to depart from the corresponding LDA values to a lesser or greater extent depending on the nature of the orbital from which the electron is removed. For instance, the values for the first ionization energies of N_2 and CO are increased by the gradient correction while the second ionization energies are in fact slightly decreased. Considering that the first ionization from N_2 or CO involves orbitals of σ -symmetry (**1a**), whereas the second ionization involves orbitals of π -symmetry (**1b**), these results can be readily explained by recalling some of the arguments presented in Sect. 3.

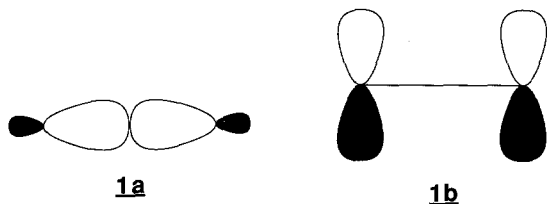


Table 3. Ionization energies (eV). First and second ionization in the given order

	HFS ^a	LDA ^a	LDA/NL ^a	Exp. ^b
N ₂	14.60	15.05	15.24	15.60
	16.6	16.95	16.81	16.98
CO	12.81	13.50	13.85	14.01
	16.71	17.17	17.01	16.53
F ₂	14.78	15.02	15.34	15.70
	18.08	18.35	18.58	18.98
H ₂ O	12.03	12.55	12.59	12.62
	13.95	14.46	14.60	14.75
NH ₃	10.06	10.62	10.76	10.88
	15.59	15.98	16.37	16.0
CH ₄	13.18	13.61	14.01	14.35
	21.20	21.50	22.00	23.00
C ₂ H ₄	10.14	10.60	10.56	10.51
	11.84	12.22	12.75	12.85

^a All calculated values from Tschinke V, Ziegler T [7]. $\alpha_x = 2/3$, except for the HFS results ($\alpha_x = .7$). Non-local functional of Ref. [4]

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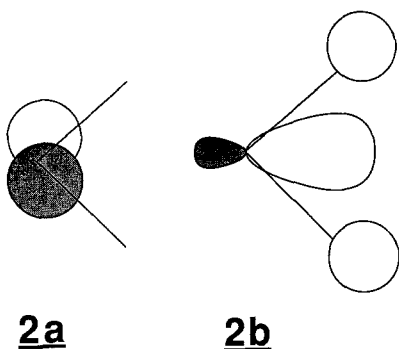
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The σ -orbital **1a** contains considerable $2s$ character, while the π -orbital **1b** is made up purely from p -orbitals due to symmetry constraints. The non-local correction is as a consequent more stabilizing for the σ -orbital **1a** where the $2s$ penetrates the core region than it is for the π -orbital **1b**. We expect thus the non-local correction to be larger for the ionization out of the σ -orbital than out of the π -orbital, and this is in fact what is observed for the N₂ and the CO molecules in Table 3. By contrast the gradient correction terms are close in magnitude for the first and second ionization energies of the F₂ molecule, involving a π^* - and a π -orbital, respectively, neither of which contain $2s$ -orbital contributions.

The results presented in Table 3 for poly-atomics can be rationalized along the same lines of reasoning presented above. We shall briefly discuss the cases of water. In the water molecule, the first ionization involves the orbital **2a**, whereas the second ionization involves the orbital **2b**. Unlike **2a**, the orbital **2b** contains a contribution from the oxygen $2s$ -orbital. Thus, as expected, we find the gradient correction to be more important for the calculated second ionization than for the first ionization. One should also note that the first ionization energy is fairly well represented by the simple LDA calculation, while the less satisfactory LDA result for the second ionization energy is significantly improved by the gradient corrections.



6. Conclusions

The HFS method represents the exchange potential $V_x^\gamma(\vec{r}_1)$ adequately at atomic radial density maxima and in the bonding regions of molecules. However, the HFS potential $V_x^\gamma(\vec{r}_1)$ is too weak in the tails of the core-shells and of the valence density. The inadequate representation of the exchange potential in the tail regions introduces two types of errors in the evaluation of bond energies which both tend to over-estimate bond strengths. The first stems from the promotion of density from the tails of the atomic core-shells to the density maximum of the valence shell on bond formation. The second is related to a transformation of parts of the atomic valence tails into the bonding region with a density maximum as the molecule is formed. The contributions from the tail regions to the exchange energy are in both cases under-estimated in the local approximation with the result that the calculated bond energies are too large.

We have carried out a detailed graphical analysis of the non-local density gradient corrections pioneered by Becke [3–5] and others [6–7]. The analysis has demonstrated how the non-local corrections improve on the calculated bond energies by rectifying the qualitatively incorrect behaviours of the local Fermi-hole function in the tail regions. The non-local correction terms are further shown to improve uniformly calculated bond energies and ionization potentials. It should be mentioned that the LDA/NL results presented here were based on LDA wave-functions. The influences of the SCF effect on non-local density functional calculations are currently under investigation [16].

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