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Statistical electron correlation – coefficients and – holes in molecules*

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Summary. Electron correlation in the H_2, LiH and BH molecules has been analyzed in terms of the statistical correlation coefficients introduced by Kutzelnigg, Del Re, and Berthier. Angular, radial (in-out), longitudinal (left-right) and transverse correlation coefficients have been evaluated from both self-consistent-field (SCF) and configuration interaction (CI) wave functions. It has been found that these coefficients reflect fairly well the correlation behavior in the molecular system. The lack of spherical symmetry in molecular densities adds new features to these correlation coefficients and this information can be useful for the study of electronic structure in molecules. The correlation hole function, Fermi and Coulomb holes in these systems have also been calculated and discussed.

Key words: Electron correlation – H_2 – LiH – BH – Statistical correlation coefficients

1 Introduction

Electron correlation is a frequently used term in quantum chemistry. It signifies the instantaneous interaction of electrons in atomic and molecular systems. Therefore it seems natural to study this correlation effect by a statistical approach. Nevertheless, the same term has long been referred to as the difference between the exact and Hartree-Fock (HF) *energies* [1] or the electron pair densities [2, 3]. In the HF scheme, due to the antisymmetrizing of the wave function, electron correlation has been partially taken into account. This part of correlation involves electrons of the same spin only. The difference between a HF pair density and a purely independent particle pair density is usually referred to as the Fermi hole. Other parts of electron correlation account mostly for the interaction of electrons with different spins and the hole produced is commonly called the Coulomb hole [4, 5]. It is clear that the statistical correlation will include both the Fermi and Coulomb holes.

Statistical correlation between electrons can be studied in a variety of ways, such as analyzing electron correlation holes [4–9] or examining the pair correlation density itself [10–15]. However, these quantities are in general functions of up to

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* Dedicated to Professor Werner Kutzelnigg on the occasion of his sixtieth birthday

six variables (the spatial coordinates of two particles) and as expected are quite complicated to visualize. There have been a few approaches proposed which can tackle this problem to certain degrees. For the pair correlation density, Banyard and coworkers [10, 16] display the pair density around a prelocated electron and thus partial correlation holes are readily shown. Another common approach is to transform the two electron positions into intracule and extracule coordinates [17] and analyze electron correlation effects through intracule and extracule densities [14–18]. The statistical correlation coefficients introduced by Kutzelnigg, Del Re, and Berthier [19] provide overall measures of correlation in the systems. These simple indices have proven to be quite valuable for analyzing electron correlation in atomic systems [20, 21].

In the present paper, we apply the ideas of Kutzelnigg et al. [19] to some linear molecules. The correlation coefficients are analyzed along with other common approaches, namely correlation hole functions, Fermi and Coulomb holes. The H_2, LiH and BH molecules have been chosen for illustration. The 3-21G and the 6-31G** basis sets [22] are used. For H_2, the two H atoms are placed at $z = \pm 0.7040a_0$. For LiH and BH, the heavier atom is set at the origin, and the H atom at $z = 3.0992a_0$ and $2.3219a_0$ respectively which corresponds to the opitimized geometry at the HF level with the 3-21G basis sets [13]. The CI wave function includes all the single and double substitutions from the ground state SCF wave function and therefore is denoted as SDCI. Hartree atomic units [23] are employed throughout this paper.

2 Statistical electron correlation coefficients

In the statistical sense electron correlation is the manner in which the electron pair density differs from the product of the one-electron densities. The spin-traced pair density is defined by:

$$D_2(\vec{r}_1, \vec{r}_2) = \int \Phi^*(\vec{x}_1, \vec{x}_2, \cdots, \vec{x}_N)\Phi(\vec{x}_1, \vec{x}_2, \cdots, \vec{x}_N) d\sigma_1 d\sigma_2 d\vec{x}_3 \cdots d\vec{x}_N, \tag{1}$$

where $\vec{x}_i = (\vec{r}_i, \sigma_i)$ is a combined space-spin coordinate of electron i. The one-electron density can be constructed from the pair density by integrating over the second particle:

$$D_1(\vec{r}_1) = \int D_2(\vec{r}_1, \vec{r}_2) d\vec{r}_2. \tag{2}$$

Both pair and one-electron densities are normalized to unity:

$$\int D_2(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 = \int D_1(\vec{r}_1) d\vec{r}_1 = 1. \tag{3}$$

Statistical correlation is measured by the difference function $c(\vec{r}_1, \vec{r}_2)$, which is given as:

$$c(\vec{r}_1, \vec{r}_2) = D_2(\vec{r}_1, \vec{r}_2) - D_1(\vec{r}_1) D_1(\vec{r}_2). \tag{4}$$

Two particles are said to be not correlated if $c(\vec{r}_1, \vec{r}_2) = 0$. In this case, the pair density of electrons 1 and 2 is equal to the product of their individual one-electron densities.

Kutzelnigg et al. [19] use concepts from probability and statistical theory to define a generalized correlation coefficient for a function $f(\vec{r})$ in position space (similar correlation coefficients may be defined in momentum space [19]):

$$\tau_f = \frac{\langle f(\vec{r}_1)f(\vec{r}_2)\rangle - \langle f(\vec{r})\rangle^2}{\langle f^2(\vec{r})\rangle - \langle f(\vec{r})\rangle^2}. \tag{5}$$

In the above equation, the expectation values of the function $f(\vec{r})$ are defined by:

$$\langle f(\vec{r}_1)f(\vec{r}_2)\rangle = \int D_2(\vec{r}_1,\vec{r}_2)f(\vec{r}_1)f(\vec{r}_2)d\vec{r}_1 d\vec{r}_2, \tag{6}$$

$$\langle f(\vec{r})\rangle = \int D_1(\vec{r})f(\vec{r})d\vec{r}. \tag{7}$$

It is obvious that when electrons are not correlated, the correlation coefficient for the function $f(\vec{r})$ will be zero. However, the inverse statement is not true, a vanishing correlation coefficient does not necessarily mean that there is no correlation. Further details will be discussed below.

2.1 *Angular correlation coefficients*

Kutzelnigg and his colleagues [19] define the correlation coefficient $\tau_{\vec{r}}$ by setting the function $f(\vec{r}) = \vec{r}$ in Eq. (5), i.e.:

$$\tau_{\vec{r}} = \frac{\langle \vec{r}_1 \cdot \vec{r}_2\rangle - \langle \vec{r}\rangle^2}{\langle \vec{r}^2\rangle - \langle \vec{r}\rangle^2}. \tag{8}$$

According to probability theory, $\tau_{\vec{r}}$ is bounded in magnitude by unity:

$$-1 \leqslant \tau_{\vec{r}} \leqslant 1. \tag{9}$$

In an atomic system, with the natural choice of the origin at the nucleus, the $\langle \vec{r}\rangle$ vanishes. The correlation coefficient defined in Eq. (8) essentially measures the angular correlation between the position vectors of two electrons:

$$\begin{aligned}\tau_\theta &= \frac{\langle \vec{r}_1 \cdot \vec{r}_2\rangle}{\langle \vec{r}^2\rangle} \\ &= \frac{\langle r_1 r_2 \cos\theta\rangle}{\langle r^2\rangle}.\end{aligned} \tag{10}$$

An even simpler angular correlation coefficient has also been used by defining $f(\vec{r}) = \vec{r}/r$ [20, 24]:

$$\tau_{\vec{r}/r} = \langle \cos\theta\rangle. \tag{11}$$

In Eq. (10), if $\vec{r}_2 = a\vec{r}_1 + \vec{b}$, it is easy to show that $\tau_\theta = 1$ or -1 depending on the sign of the constant a. When $\tau_\theta = 1$, the position vectors of the two electrons in a pair are expected to coincide and a perfect positive correlation results. On the other hand, when $\tau_\theta = -1$, the two vectors will always be expected to have opposite directions and this defines the perfect negative correlation. A value of $\tau_\theta = 0$ can mean either no angular correlation at all between the two position vectors or that they correlate in special ways, for instance, the two vectors always form angles $\theta = \pm\, \pi/2$.

In molecules, the choice for the origin is no longer straightforward and the interpretation of $\tau_{\vec{r}}$ as an indicator of the angular correlation is not quite accurate. Since the origin of the system is allowed to shift in Eq. (8), $\tau_{\vec{r}}$ still can be related to the angular correlation of two electrons by introducing new position vectors (with $\vec{r}\,' = \vec{r} - \langle \vec{r} \rangle$). However, the angle formed by the new vectors is in general not the same as that defined by $\vec{r}_1$ and $\vec{r}_2$ and this will cause difficulties for the comparison of $\tau_{\vec{r}}$ between two sets of wave functions. (Note that the momentum space counterpart does not share this problem because the origin is well defined for atoms and molecules alike [25] and $\langle \vec{p} \rangle = 0$). Nevertheless, for the sake of simplicity, we still call $\tau_{\vec{r}}$ the angular correlation coefficient and use $\tau_{\vec{r}}$ and τ_θ interchangeably in the following discussion.

The angular correlation coefficients of H_2 have been calculated from full CI wave functions with 3-21G and 6-31G** basis sets [22] and tabulated in Table 1. No corresponding values from a HF level treatment are shown in the table. They are simply zero because there is no correlation in this case. With the full CI wave functions, the two electrons in H_2 undergo negative angular correlation. The two position vectors are more likely to have angles between $\pi/2$ and $3\pi/2$. With polarization functions included in the basis sets, the angular correlation coefficient becomes even smaller. The value with the 6-31G** basis set is closer to the one calculated from a much better correlated wave function [26], as shown in Table 1.

The angular correlation coefficients of LiH and BH are shown in Table 2 for SCF wave functions and in Table 3 for SDCI wave functions. In LiH and BH, there is nonvanishing angular correlation even at the HF level because of the presence of Fermi correlation between electrons of the same spin. It is interesting to note that this angular correlation coefficient decreases in absolute value for LiH and increases for BH from the HF to SDCI treatments with the 3-21G basis sets. The large negative angular correlation of LiH at the SCF level is largely due to its electronic structure. Previous studies [15] show that there is substantial charge transfer in LiH at the SCF level. The molecule hence displays quite a large amout of ionic character (Li^+H^-). Electron correlation has been found to shift electrons from H back to Li. This causes redistribution of electrons in the molecular system and the main effect of introducing elecron correlation is to relax the angular coupling of the electrons. The lack of flexibility of the 3-21G basis set is another reason for decreasing negative angular correlation in LiH comparing the SDCI correlation coefficients with the HF ones. When the more flexible and extended 6-31G** basis sets have been employed, both LiH and BH show the same tendency for the angular correlation change; i.e., the angular correlation coefficients become smaller as electron correlation has been taken into consideration.

Table 1. Electron correlation coefficients for H_2 from the full CI wave functions

	3-21G	6-31G**	KW†
τ_θ	– 0.07851	– 0.08124	– 0.10597
τ_z	– 0.18547	– 0.16412	– 0.15605
τ_b	– 0.07370	– 0.07537	– 0.07234
$\tau_{1/r}$	0.02788	0.03302	
τ_r	– 0.07620	– 0.10156	

†: Calculated from the expectation values in [26]

Table 2. Electron correlation coefficients for LiH and BH from the SCF wave functions

	LiH		BH	
	3-21G	6-31G**	3-21G	6-31G**
τ_θ	– 0.12761	– 0.13000	– 0.06867	– 0.07054
τ_z	– 0.22344	– 0.22643	– 0.12180	– 0.12534
τ_b	– 0.10802	– 0.11268	– 0.08222	– 0.08268
$\tau_{1/r}$	– 0.09347	– 0.08908	– 0.06846	– 0.06557
τ_r	– 0.24503	– 0.25079	– 0.11540	– 0.11676

Table 3. Electron correlation coefficients for LiH and BH from the SDCI wave functions

	LiH		BH	
	3-21G	6-31G**	3-21G	6-31G**
τ_θ	– 0.12472	– 0.13548	– 0.08121	– 0.08908
τ_z	– 0.22281	– 0.22818	– 0.12356	– 0.12906
τ_b	– 0.14292	– 0.14540	– 0.09119	– 0.09301
$\tau_{1/r}$	– 0.09360	– 0.08916	– 0.06856	– 0.06579
τ_r	– 0.24564	– 0.25393	– 0.12798	– 0.13005

2.2 Radial correlation coefficients

The radial correlation coefficient can be introduced in this case as a measure for the in-out interaction:

$$\tau_{\vec{r}} = \frac{\langle r_1 r_2 \rangle - \langle r \rangle^2}{\langle r^2 \rangle - \langle r \rangle^2} \tag{12}$$

A similar quantity associated with the radial correlation is also defined by setting $f(\vec{r}) = 1/r$. The correlation coefficient $\tau_{1/r}$ is obtained by replacing r with $1/r$ in Eq. (12). These two radial correlation indices are supposed to show similar behavior, but the following numerical values for H_2 provide an exception. This may result from the fact that r and $1/r$ weight the space differently. The former one will emphasize the outer regions more, whereas the latter tends to weight the inner regions heavily.

For molecular systems, the radial quantities are origin dependent. The correlation coefficient, without exception, is also dependent on the choice of origin. Even though the radial correlation coefficient is not uniquely defined in molecular systems, it is still quite useful for making much easier the comparison of correlation behavior in atomic and molecular systems.

In Table 1, the radial correlation coefficients, τ_r and $\tau_{1/r}$, are given for H_2 with the origin at the bond midpoint and in Tables 2 and 3 for LiH and BH with origins on the respective heavier atom. The calculated τ_r and $\tau_{1/r}$ for H_2 vanish at the SCF level and show opposite changes for the full CI treatment. Actually, electron correlation in H_2 shows two main effects relating to the radial electron motion. There is more covalent nature in the CI density and this contributes to a positive correlation coefficient because the origin is located at the center of the two atoms. At the same time, inclusion of Coulomb correlation of the electrons will eliminate the possibility of two electrons being at the same location (which results in a positive radial correlation coefficient) to a great extent and the electrons will tend to have different radii. As τ_r weights more the outer region, it will likely be negative and is so for H_2 (full CI), LiH and BH. The coefficient $\tau_{1/r}$ depends on the inner regions more heavily and it is found to be positive for H_2 and negative for LiH and BH. Electron correlation has been found to cause much smaller radial pair shifts in LiH than in BH (see Fig. 11 in [14]), which is in good agreement with the finding from the radial correlation coefficient. The radial correlation coefficient changes are significantly smaller in LiH than in BH from the SCF (Table 2) to the SDCI (Table 3) treatments. Note that different choices of the origin may lead to different values for the radial correlation coefficients, but the information revealed will be similar.

2.3 *Longitudinal correlation coefficients*

For molecular systems, electron pair densities display anisotropy. Even though the angular and radial correlation coefficients are useful in these situations, other correlation coefficients may be more appropriate. For linear molecules, due to the cylindrical symmetry, longitudinal, and transverse pair densities are convenient for analysis. By introducing the cylindrical coordinates (b, z, ω), the pair density $D_2(\vec{r}_1, \vec{r}_2)$ can be projected onto the longitudinal and transverse directions. These projected pair densities are called longitudinal and transverse pair densities, respectively:

$$L_2(z_1, z_2) = \int D_2(\vec{r}_1, \vec{r}_2) b_1 b_2 db_1 d\omega_1 db_2 d\omega_2$$

$$= 4\pi^2 \int D_2(\vec{r}_1, \vec{r}_2) b_1 b_2 db_1 db_2, \tag{13}$$

$$T_2(b_1, b_2) = \int D_2(\vec{r}_1, \vec{r}_2) dz_1 d\omega_1 dz_2 d\omega_2$$

$$= 4\pi^2 \int D_2(\vec{r}_1, \vec{r}_2) dz_1 dz_2. \tag{14}$$

Similarly, the longitudinal and transverse one-electron densities are defined by:

$$L_1(z_1) = 2\pi \int D_1(\vec{r}_1) b_1 db_1, \tag{15}$$

$$T_1(b_1) = 2\pi \int D_1(\vec{r}_1) dz_1. \tag{16}$$

Following the same procedure, Kutzelnigg et al. [19] define the longitudinal correlation coefficient τ_z by:

$$\tau_z = \frac{\langle z_1 z_2 \rangle - \langle z \rangle^2}{\langle z^2 \rangle - \langle z \rangle^2}. \tag{17}$$

For linear molecules, the longitudinal direction coincides with the bonding axis. As a result, the longitudinal correlation coefficient is pertinent to show the intertwined information regarding chemical bonding and electron correlation. By comparing the τ_z values for LiH from SCF and SDCI wave functions, we see a decrease in magnitude for this quantity with the 3-21G basis set. The explanation for this change is same as that for the angular correlation discussion for this same molecule. Electron correlation causes electron transfer from H back to Li and thus there is less longitudinal correlation from the SDCI treatment. Less flexbility of the 3-21G basis set is another reason. With the better basis set 6-31G**, this longitudinal correlation coefficient decreases when electron correlation is included.

2.4 Transverse correlation coefficients

The transverse correlation coefficient has been introduced to measure the correlation on the equatorial plane. It is written as:

$$\tau_b = \frac{\langle b_1 b_2 \rangle - \langle b \rangle^2}{\langle b^2 \rangle - \langle b \rangle^2}. \tag{18}$$

The numerical values of τ_z for H_2, LiH, and BH are tabulated in Tables 1, 2, and 3, respectively. It has been found that there are substantial increases of negative transverse correlation for H_2, BH and especially LiH when SDCI instead of SCF wave functions are used.

Compared with those computed at the 3-21G basis set, the higher angular functions in the 6-31G** basis sets clearly enhance the negative transverse correlation in the H_2 molecule. Both the values are not very far from the one computed from the expectation values reported by Kolos and Wolniewicz [26].

3 Electron correlation holes

If a reference electron is located at position $\vec{r}_1$, the correlation hole function is defined by [4, 5, 12]:

$$\xi(\vec{r}_1, \vec{r}_2) = \frac{c(\vec{r}_1, \vec{r}_2)}{D_1(\vec{r}_2)} = \frac{D_2(\vec{r}_1, \vec{r}_2)}{D_1(\vec{r}_2)} - D_1(\vec{r}_1). \tag{19}$$

Thus defined correlation hole function allows us to study both the Fermi and Coulomb correlations. When the pair density is predicted with the HF wave function, the corresponding correlation hole involves electrons of the same spin only, i.e. only Fermi correlation. With CI type wave functions, ξ will recover both Fermi and Coulomb correlations.

Generally, the correlation hole function in molecules does not display spherical symmetry. The anisotropic holes are commonly displayed [15, 16]. For linear molecules, longitudinal and transverse correlation holes can be introduced.

The correlation hole function may be alternatively introduced through probability theory. The conditional one-electron density is given as the pair densities divided by the regular one-electron density; i.e.:

$$L_1^c(z_1, z_2) = L_2(z_1, z_2)/L_1(z_2) \tag{20}$$

for the conditional longitudinal charge density and:

$$T_1^c(b_1, b_2) = T_2(b_1, b_2)/T_1(b_2) \tag{21}$$

for the conditional transverse charge density.

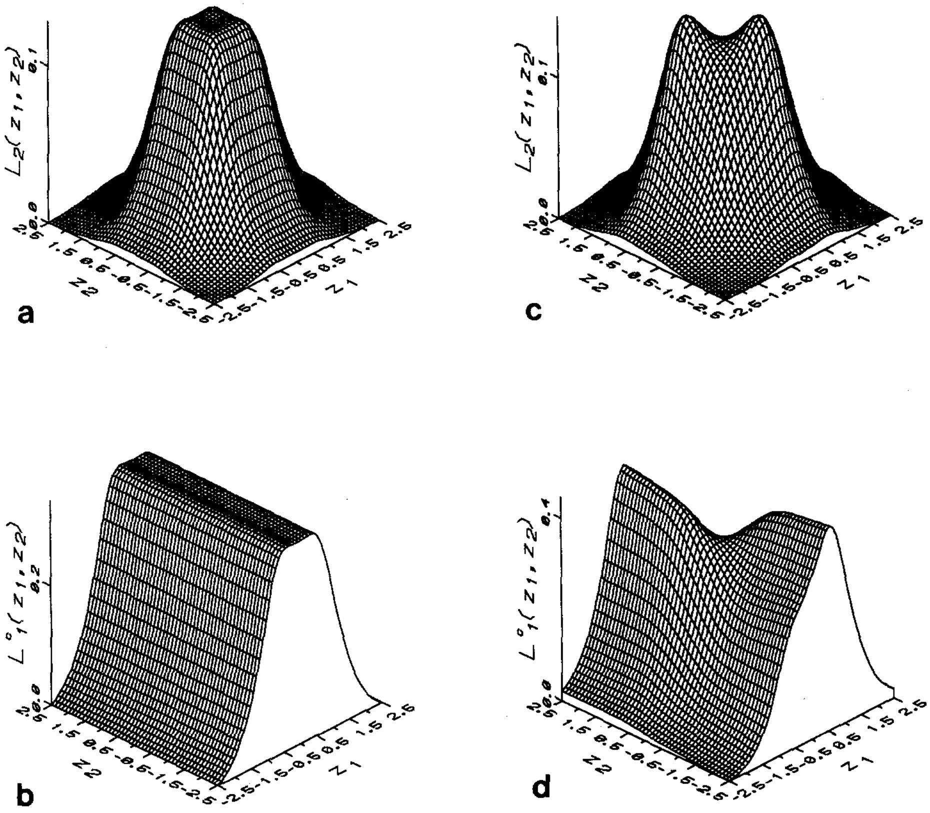

Fig. 1a–d. The longitudinal pair density (**a**) and conditional longitudinal one electron density (**b**) of H_2 of at the SCF level. Their full CI counterparts are presented in (**c**) and (**d**), respectively

The correlation hole in this case is simply the difference between the conditional one-electron density and the regular one-electron density, same as that defined by McWeeny [4, 5]. The longitudinal correlation hole is written as:

$$\xi^L(z_1, z_2) = L_1^c(z_1, z_2) - L_1(z_1), \tag{22}$$

and similarly, the transverse correlation hole is written as:

$$\xi^T(b_1, b_2) = T_1^c(b_1, b_2) - T_1(b_1). \tag{23}$$

Figure 1a shows the longitudinal pair density $L_2(z_1, z_2)$ of H_2 at the HF level. There are four peaks located at the diagonal and off-diagonal positions. The densities at the diagonal positions signify two electrons having the same z coordinate, whereas the densities at the off-diagonal positions show the probability of two electrons at different centers. The former peaks result from the ionic electron configuration (H^-H^+), and the latter peaks from the covalent configuration. The corresponding conditional charge density is displayed in Fig. 1b, the electron charge density of the electron (with z_1 coordinate) is not dependent on the position (z_2) of the second electron, as revealed by the vanishing correlation coefficient in

Sect. 2. This means that in the HF treatment, H_2 is an exacly independent system, which is quite clear because there is no Fermi correlation present in the single state of a two-electron system.

In Fig. 1c, the longitudinal pair density from the SDCI wave function is displayed. There is a large difference between this figure and Fig. 1a. The two off-diagonal peaks have been reproduced here. However, the diagonal peaks shrink to shoulders, which implies that the weight of the ionic configuration decreases. Figure 1d shows the conditional longitudinal charge density. We see clearly the correlation between the two electrons. The charge density of one electron (with z_1 as coordinate) changes with the position (z_2) of the second electron. There is a strong tendency for them not to be situated on the same center.

The longitudinal pair density of LiH with the HF wave function is shown in Fig. 2a. The diagonal peaks, at about (0, 0) and ($3a_0$, $3a_0$), are readily assigned to pairs on the Li and H atoms, respectively. The pairs arising from electrons on different centers account for the two off diagonal peaks (0, $\pm 3a_0$). The conditional longitudinal density is shown in Fig. 2b. We see that due to the Fermi correlation, the conditional charge densities of one electron is dependent on the position of the second electron even at the HF level. However, it seems that Fermi correlation only shows a large effect in the vicinity of the Li nucleus. The other parts still exhibit essentially independent behavior. The Fermi correlation decreases the probability to find simultaneously two electrons around the Li atom. The Fermi hole is clearly seen at (0, 0) in Fig. 2c.

The conditional longitudinal charge density of LiH with the SDCI wave function is shown in Fig. 2e. Visible changes happen at the position ($3a_0$, $3a_0$). The density at this point decreases as compared with that in Fig. 2b. This turns it into a saddle point. Another small change happens at (0, $3a_0$), the density at this point increases from the SCF to the SDCI treatments. Note that the ridge in the neighborhood of (0, $3a_0$) is flat in the SCF case (Fig. 2b) and is slightly concave in the SDCI (Fig. 2e). These observations imply that with inclusion of Coulomb correlation, the probability to find two electrons simultaneously around the H atom decreases, whereas the probability to locate two electrons on different centers increases. This also demonstrates that in the HF treatment, the ionic configuration has been overestimated, which is in agreement with the findings from the analysis of the correlation coeffcients.

The total correlation hole function is displayed in Fig. 2f. Besides the Fermi hole seen in Fig. 2c at (0, 0), a shallow hole is found at ($3a_0$, $3a_0$), the location of H. It is largely due to Coulomb correlation between σ bonding electrons around the H atom.

The longitudinal correlation in BH is displayed in Fig. 3a–3f. Compared with the LiH densities, the BH counterparts are more compact due to the higher nuclear charge of B and less ionic character for its electronic structure. Other features include a significant accumulation of densities at the off-bonding side of B and sharp changes of the pair density around the B nucleus (0, 0), as shown in Fig. 3a. The strong Fermi correlation leads to a substantial decrease of density around the B nucleus, especially in the off-bond directions (see Fig. 3c). No visible Fermi correlation is found around the H nucleus ($2.3a_0$, $2.3a_0$) at the SCF level. At the SDCI level, the longitudinal pair density is predicted to be broader and the correlation to be extended farther from the B nucleus. This observation is in line with the previous study [14]. Around the H nuclear position ($2.3a_0$, $2.3a_0$), Coulomb correlation results in a shallow hole (Fig. 3f).

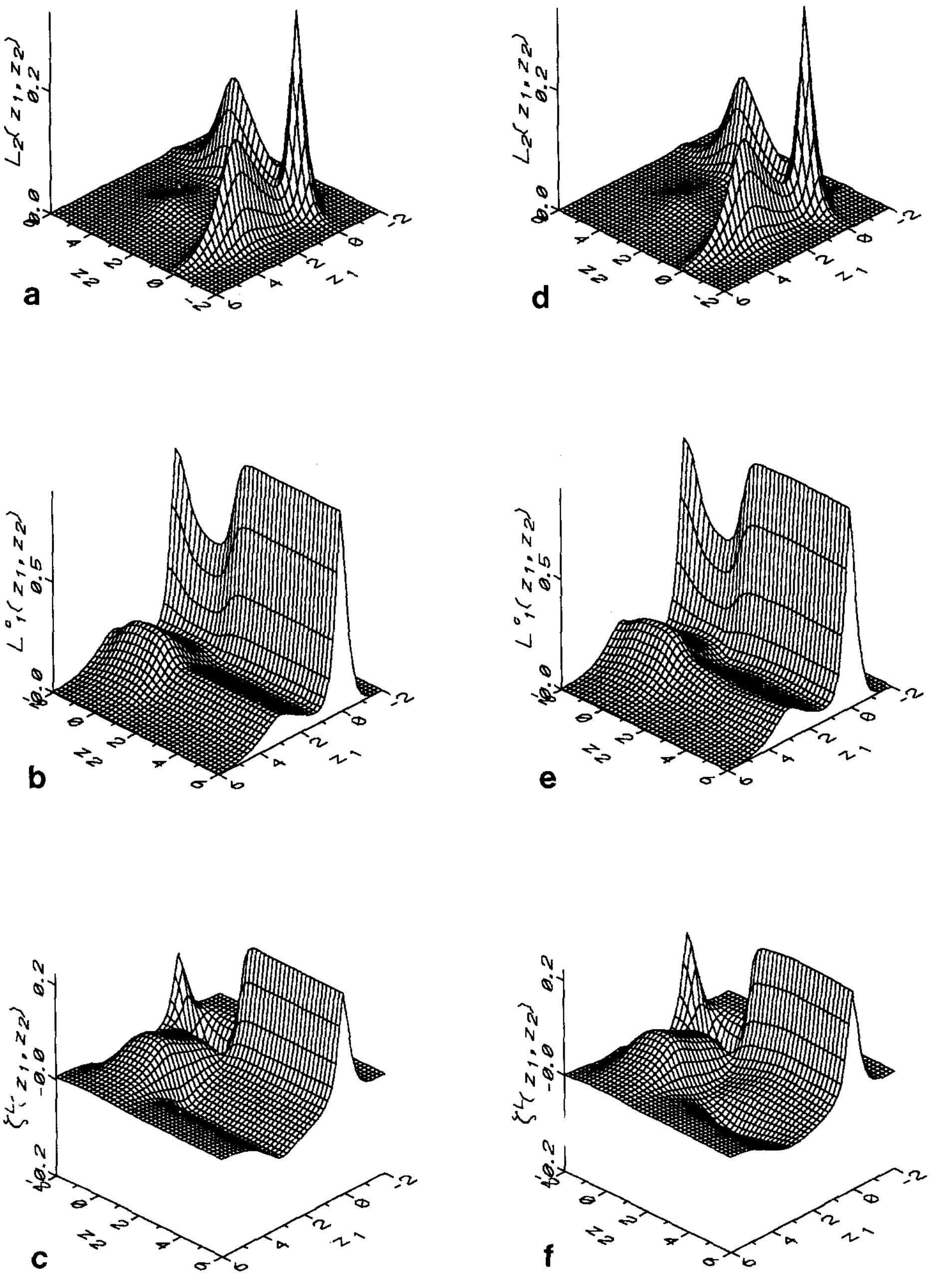

Fig. 2a–f. The longitudinal pair density (**a**), conditional longitudinal one electron density (**b**), the longitudinal Fermi hole (**c**) of LiH at the SCF level. Their SDCI counterparts are presented in (**d**), (**e**) and (**f**) (shows both Fermi and Coulomb holes), respectively

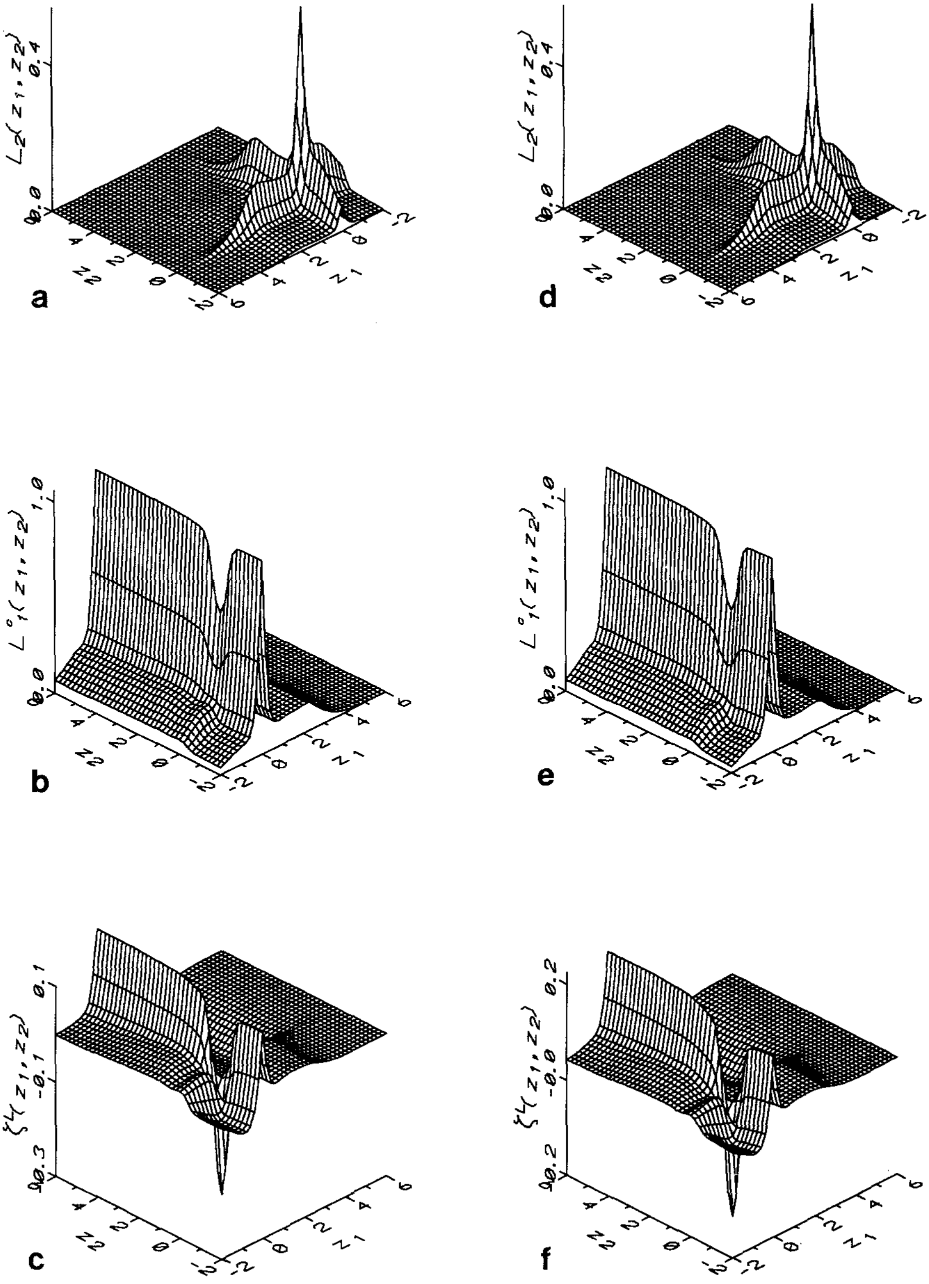

Fig. 3a–f. The logitudinal pair density (a), conditional longitudinal one electron density (b), the longitudinal Fermi hole (c) of BH at the SCF level. Their SDCI counterparts are presented in (d), (e) and (f) (shows both Fermi and Coulomb holes), respectively

4 Conclusion

The statistical electron correlation coefficients have been calculated for three simple linear molecules. It has been shown that these numerical correlation indices can reflect the electron motions in complex systems. The correlation hole function provides a visible approach to the same problem. The former is easy to use and to generalize, whereas the latter has its own merits. The pictorial approach of the latter could bring such an abstract concept as electron correlation closer to chemical intuition.

Here we have presented a preliminary study of the statistical correlation coefficients introduced by Kutzelnigg et al. [19] to molecular systems. Since electron correlation analysis requires high quality basis sets and more sophisticated treatments, in our future work, both the one- and N-particle basis sets and their effects on the correlation coefficients will be investigated.

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