

# Electron correlation studies by means of local-scaling transformations and electron-pair density functions\*

Elmer G. Valderrama<sup>†</sup> and Jesus M. Ugalde\*

Kimika Fakultatea, Euskal Herriko Unibertsitatea, Posta Kutxa 1072,  
20080 Donostia, Euskadi, Spain

E-mail: ugalde@sq.chu.es

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Electron correlation is one long standing problem of computational electronic structure theory. Even more, with the advent of the density functional theory and, in particular, with its Kohn–Sham implementation, the separation of the non-dynamical and dynamical components of the electron correlation has become an unavoidable requirement towards construction of reliable exchange-correlation functionals. In this paper, we address the analysis of the separation of the non-dynamical and dynamical electron correlation effects from two complementary viewpoints, namely, analysis of the correlation energy components and the analysis of the electron-pair density. The former approach will make use of the local-scaling transformations and the latter will be based on the study of intracule and extracule densities.

**KEY WORDS:** intracule, electron correlation, local scaling, Density Functional Theory, electron pair density

## 1. Introduction

The significance of electron correlation can hardly be overlooked in current quantum chemical studies. Although it has become customary for the practical user to include a post Hartree–Fock (HF) procedure to account for improved energy results in structure and reactivity studies, the harmful of such practices has been warned by several theoretical studies. This problem may become even more serious due to the complex structure of the electron–electron interaction, a phenomenon that is intuitively grasped by a layman but that still hides its own secrets.

Consider the usual HF level as a reference state. It is a common practice to consider the HF wave function as both a good first order approximation to the exact ground state and an appropriate *uncorrelated* reference state for

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\*Corresponding author.

highly correlated methods [1]. Although this fact is widely recognized to hold for most systems at equilibrium and devoid of any near-degeneracy effects, when the system presents a pseudo-degenerate single-determinant wave function the usual energy definition of electron correlation advanced by Löwdin [2] does not arise from purely short-range electron–electron interactions. When the HF reference state fails to afford a reasonable physical description of the system, the straight approach is to include all those degenerate (or near-degenerate) states in a self-consistent field (SCF) procedure as put forward by Ruedenberg and Roos [3,4] (CAS-SCF, complete active space SCF). As a consequence, the usual energy-based definition of electron correlation, counted from the HF state, can be regarded as a quantity composed from a system-specific, non-dynamical contribution and a non-specific, and hence, in a sense, *universal* dynamical contribution [5]. The non-dynamical correlation component is thought to arise from the long-range correlation effects resulting from the strong interaction between the HF state and the closely lying pseudo-degenerate states and can be *loosely* defined by

$$E_{\text{nd}} = E_{\text{CASSCF}} - E_{\text{HF}}. \quad (1)$$

The shortcoming of this definition is that an uncontrollable number and type of virtual orbitals are introduced in the CAS-SCF method so that the resulting non-dynamical correlation energy is contaminated by the dynamical correlation energy component [6]. The effect is also present in current formulations of single-reference density functional theory and has been studied as part of the problem of fractionally occupied orbitals [7] and the broken symmetry problem [8]. Recently, the problem of selecting the appropriate set of virtual orbitals for combining multireference wave functions and density functional methods has been addressed by several authors [9]. Other alternatives to estimate properly the importance of the non-dynamical effects include the consideration of a functional for the non-dynamical correlation energy [10], the partition of the electron–electron operator [11], and the partition of electron correlation energy [12,13].

In addition to the energy-based studies on electron correlation it is useful to resort to the analysis of the electron-pair distributions in order to afford quantitative measures of the long and short range effects of electron–electron interactions in a given system. In particular the electron intracule  $I(\mathbf{u})$  and extracule  $E(\mathbf{R})$  densities characterize the distribution of a pair of electrons in atoms and molecules [14,15] and represent the probability density functions for the relative vector  $\mathbf{r}_i - \mathbf{r}_j$  and center-of-mass vector  $(\mathbf{r}_i + \mathbf{r}_j)/2$  to be  $\mathbf{u}$  and  $\mathbf{R}$ , respectively.

$$I(\mathbf{u}) = \int \Gamma(\mathbf{r}_1, \mathbf{r}_2) \delta(\mathbf{u} - \mathbf{r}_1 + \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (2)$$

$$E(\mathbf{R}) = \int \Gamma(\mathbf{r}_1, \mathbf{r}_2) \delta\left(\mathbf{R} - \frac{\mathbf{r}_1 + \mathbf{r}_2}{2}\right) d\mathbf{r}_1 d\mathbf{r}_2, \quad (3)$$

where  $\Gamma(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \int |\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_3 \dots d\mathbf{r}_N$  is the spin-traced two-body density matrix and,  $\delta$  stands for the Dirac's delta function. The two-electron character of these quantities combined with the low dimensionality have inspired the work of several groups in order to unveil the nature of electron–electron interactions in a elegant and intelligible manner [16]. These quantities have been analyzed at the HF level in terms of their topological properties [17] as well as in terms of the topology of their Laplacians for atoms [18] and for molecules [19]. When they are evaluated at a higher level of theory, they provide valuable information about the electron correlation present in atomic and molecular systems. In doing so, the nature of the Coulomb hole can be revealed [20,21], the effect of molecular electron correlation on anisotropic  $E(\mathbf{R})$  and  $I(\mathbf{u})$  can be displayed [22] and an illuminating topological picture of the detailed electron–electron Coulomb interaction can be provided [23,24]. Electron-pair densities have been used as starting entities for the design and interpretation of current density functionals [25,26] and for the calculation of exact exchange–correlation potentials [27].

These quantities have been also analyzed in relation to the importance of radial and angular correlation for two-electron systems [28]. Remarkable properties have been formulated on the upper bound constraints for HF and exact intracule densities at  $\mathbf{u} = 0$  [29,30]. Other derived quantities such as the electron–electron counterbalance density  $d(0)$  and the electron coalescence density  $h(0)$  which are the spherically averaged densities for  $E(\mathbf{R})$  and  $I(\mathbf{u})$ , respectively, evaluated at origin, provide further insights into the nature of electron correlation [28,31].

In this paper, we address the analysis of electron correlation from the energetic point of view and from the electron-pair distribution approach. The first approach will make use of the local-scaling transformations and the second will be based on the study of intracule and extracule densities.

## 2. Local-scaling transformations and a decomposition scheme for the correlation energy

A *local-scaling* transformation is a generalization of the well-known *uniform-scaling* transformations  $\mathbf{f}(\mathbf{r}) = \lambda\mathbf{r}$ , where the scaling parameter  $\lambda$  is just a constant. In the case of local-scaling transformations,  $\lambda$  is a function of  $\mathbf{r}$  that modifies the position vector  $\mathbf{r}$  according to

$$\mathbf{f}(\mathbf{r}) = \lambda(\mathbf{r})\mathbf{r} = (\lambda(\mathbf{r})x, \lambda(\mathbf{r})y, \lambda(\mathbf{r})z). \quad (4)$$

Consider applying a local-scaling transformation to an arbitrary  $N$ -electron wave function,  $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ . The resulting new wave function  $\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  is given by

$$\begin{aligned}\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) &= \widehat{f} \cdots \widehat{f} \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \\ &\quad \text{(N-times)} \\ &= \prod_{i=1}^N [J(\mathbf{f}_i, \mathbf{r}_i)]^{\frac{1}{2}} \Psi(\mathbf{f}_1, \mathbf{f}_2, \dots, \mathbf{f}_N),\end{aligned}\quad (5)$$

where the transformation operator  $\widehat{f}$  denotes the effect of the local-scaling transformation on the function  $\Psi$ , and the Jacobian of the transformation,  $J(\mathbf{f}_i, \mathbf{r}_i)$ , is given by the relation

$$d\mathbf{f}_i = J(\mathbf{f}_i, \mathbf{r}_i) d\mathbf{r}_i, \quad (6)$$

and is determined by the explicit form of  $\lambda(\mathbf{r})$ . Notice that the transformed wave function  $\Phi$  conserves the normalization and that the one-electron densities,  $\rho_\Psi$  and  $\rho_\Phi$ , associated to the *generating* wave function  $\Psi$  and the *target* wave function  $\Phi$ , respectively, are related by

$$\rho_\Phi(\mathbf{r}) = J(\mathbf{f}, \mathbf{r}) \rho_\Psi(\mathbf{f}), \quad (7)$$

a result obtained simply by applying equations (5) and (6) and the usual definition

$$\rho_\Phi(\mathbf{r}) = \int |\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3, \dots, d\mathbf{r}_N. \quad (8)$$

So far the explicit form of scaling function  $\lambda(\mathbf{r})$  has not been given and a particular choice is to define it as follows

$$\lambda(\mathbf{r}) = \frac{f(\mathbf{r})}{r}, \quad (9)$$

so that the Jacobian of the transformation is given by

$$J(\lambda(\mathbf{r})\mathbf{r}; \mathbf{r}) = \begin{bmatrix} \frac{\partial \lambda(\mathbf{r})_x}{\partial x} & \frac{\partial \lambda(\mathbf{r})_y}{\partial x} & \frac{\partial \lambda(\mathbf{r})_z}{\partial x} \\ \frac{\partial \lambda(\mathbf{r})_x}{\partial y} & \frac{\partial \lambda(\mathbf{r})_y}{\partial y} & \frac{\partial \lambda(\mathbf{r})_z}{\partial y} \\ \frac{\partial \lambda(\mathbf{r})_x}{\partial z} & \frac{\partial \lambda(\mathbf{r})_y}{\partial z} & \frac{\partial \lambda(\mathbf{r})_z}{\partial z} \end{bmatrix} = \frac{1}{r^3} \mathbf{r} \cdot \nabla_{\mathbf{r}} f^3(\mathbf{r}). \quad (10)$$

Substituting equation (10) into equation (7) and using polar coordinates,  $\mathbf{r} = (r, \theta, \phi)$ , we obtain a first order differential equation for the transformation function  $f(\mathbf{r})$ ,

$$\frac{df(r, \theta, \phi)}{dr} = \frac{r^2}{f^2(r, \theta, \phi)} \frac{\rho_\Phi(r, \theta, \phi)}{\rho_\Psi(f(r, \theta, \phi), \theta, \phi)}. \quad (11)$$

For the case of spherically-symmetric or spherically-averaged densities, the local-scaling function  $\lambda(r, \theta, \phi)$  reduces to  $\lambda(r)$  and, hence, equation (11) is simplified to

$$\frac{df(r)}{dr} = \frac{r^2}{f^2(r)} \frac{\rho_\Phi(r)}{\rho_\Psi(f(r))}. \quad (12)$$

It is clear that if the given initial density  $\rho_\Psi$  is kept fixed, for instance, it is set to be the HF density, and the final density is chosen from a given set, say, of correlated electron densities  $\{\rho_{\text{CISD}}, \rho_{\text{FCI}}, \rho_{\text{MCSCF}}, \dots\}$ , then different solutions of equation (12), namely,  $\{f_{\text{CISD}}(r), f_{\text{FCI}}(r), f_{\text{MCSCF}}(r), \dots\}$ , will be found. This way, the transformed coordinate  $\mathbf{f}(\mathbf{r})$  is determined from the final density  $\rho(r)$  and, by means of equation (5), the transformed wave function can be evaluated. In fact, from equations (5) and (6), it can be shown that the transformed wave function yields the final electron density by quadrature

$$\begin{aligned} & \int |\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3, \dots, d\mathbf{r}_N \\ &= \int \prod_{i=1}^N [J(\mathbf{f}_i, \mathbf{r}_i)] |\Psi(\mathbf{f}_1, \mathbf{f}_2, \dots, \mathbf{f}_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3, \dots, d\mathbf{r}_N \\ &= \frac{\rho_\Phi(\mathbf{r}_1)}{\rho_\Psi(\mathbf{f}_1)} \int \prod_{i=2}^N \left[ \frac{\rho_\Phi(\mathbf{r}_i)}{\rho_\Psi(\mathbf{f}_i)} \right] |\Psi(\mathbf{f}_1, \mathbf{f}_2, \dots, \mathbf{f}_N)|^2 \prod_{i=2}^N \left[ \frac{\rho_\Psi(\mathbf{f}_i)}{\rho_\Phi(\mathbf{r}_i)} \right] d\mathbf{f}_2 d\mathbf{f}_3, \dots, d\mathbf{f}_N \\ &= \frac{\rho_\Phi(\mathbf{r}_1)}{\rho_\Psi(\mathbf{f}_1)} \int |\Psi(\mathbf{f}_1, \mathbf{f}_2, \dots, \mathbf{f}_N)|^2 d\mathbf{f}_2 d\mathbf{f}_3, \dots, d\mathbf{f}_N = \rho_\Phi(\mathbf{r}). \end{aligned} \quad (13)$$

In figure 1 a schematic representation of the local-scaling transformation is shown: right-hand side arrows determine  $f(r)$  by equation (12) from the given densities, and the left hand arrows apply the found transformation function on the initial wave function to yield a transformed wave function that yields the final density, from which the transformation function was found. This is the central point of the local-scaling transformations: to produce a new wave function that yields a target electron density from a preceding (generating) wave function. This fact can be further exploited in the framework of density functional theory and a *constructive* procedure to design density functionals of high accuracy has been proposed [32, 33]. In the following section we will denote the total energies obtained from a generating wave function and its associated final density by explicitly writing them down as functionals of these entities. Thus, the functional  $E[\Psi^{\text{HF}}, \rho_{\text{FCI}}]$  stands for the energy obtained from a generating HF wave function such that the locally scaled, transformed HF wave function yields the final full configuration-interaction (FCI) density.

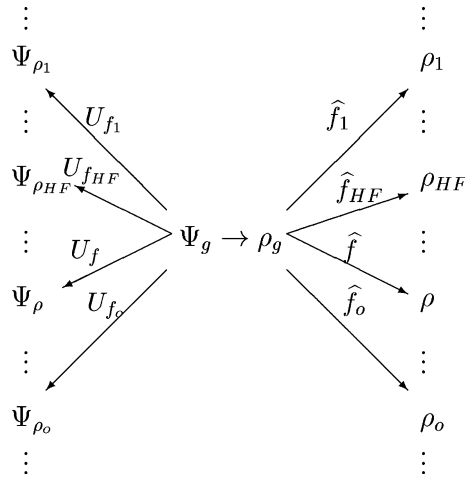


Figure 1. Schematic representation of local-scaling transformations of a given wave function  $\Psi_g$ : r.h.s. arrows represent operators  $\hat{f}$  determined by the two electron densities ( $\rho_g$  and  $\rho_f$ ). The corresponding unitary operator  $U_f$  acts on the wave function  $\Psi_g$  (l.h.s. arrows) yielding a transformed wave function  $\Psi_f$  associated to the chosen  $\rho_f$ .

### 2.1. A decomposition scheme for the correlation energy

Regarding the analysis of electron correlation energy, local-scaling transformations can readily be used as a unambiguous criterion to assess the relative importance of non-dynamical correlation in quantum systems [13]. The usual *quantum mechanical* definition of electron correlation energy is

$$E_c = E_{\text{exact}} - E_{\text{HF}}, \quad (14)$$

which can be rewritten as the density-functional expression

$$E_c = E[\Psi^{\text{exact}}, \rho_{\text{exact}}] - E[\Psi^{\text{HF}}, \rho_{\text{HF}}]. \quad (15)$$

Notice that this energy difference is obtained from energies associated to both different wave functions and different electron densities. As a consequence, the electron correlation energy cannot be formulated as a functional of the density, in general. Recall that the alternative *density-functional* electron correlation defined by

$$E_c^{\text{DFT}} = E[\Psi^{\text{exact}}, \rho_{\text{exact}}] - E_x[\Psi^{\text{KS}}, \rho_{\text{exact}}], \quad (16)$$

where  $\Psi^{\text{KS}}$  is the single-determinant Kohn–Sham wave function and the subscript  $x$  indicates that the energy  $E_x$  only includes the *exact* exchange energy

evaluated with the Kohn–Sham orbitals,  $\phi_i(\mathbf{r})$ ,

$$-\frac{1}{2} \sum_{\substack{i,j=1 \\ \text{spin } j || \text{spin } i}}^N \int \frac{\phi_i^*(\mathbf{r})\phi_i(\mathbf{r}')\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (17)$$

can certainly be regarded as a density functional. The relationship between  $E_c$  and  $E_c^{\text{DFT}}$  will be established below.

Now we can proceed to propose a energy decomposition that will reveal the dynamical and non-dynamical character of the quantum-mechanical electron correlation energy. Figure 2 depicts the proposed partitioning scheme where the notation  $E[\Psi, \rho]$  means the energy evaluated with a wave function  $\Psi$  that yields density  $\rho$ . It is clear that the differences

$$E_d^{\text{I}} = E[\Psi^{\text{exact}}, \rho_{\text{HF}}] - E[\Psi^{\text{HF}}, \rho_{\text{HF}}] \quad (18)$$

and

$$E_{\text{nd}}^{\text{I}} = E[\Psi^{\text{exact}}, \rho_{\text{exact}}] - E[\Psi^{\text{exact}}, \rho_{\text{HF}}], \quad (19)$$

which represents decomposition along Path I (figure 2), will sum up to the whole electron correlation energy. The decomposition along Path II will give

$$E_d^{\text{II}} = E[\Psi^{\text{exact}}, \rho_{\text{exact}}] - E[\Psi^{\text{HF}}, \rho_{\text{exact}}] \quad (20)$$

and

$$E_{\text{nd}}^{\text{II}} = E[\Psi^{\text{HF}}, \rho_{\text{exact}}] - E[\Psi^{\text{HF}}, \rho_{\text{HF}}]. \quad (21)$$

The leading feature of this partitioning scheme is that the non-dynamical component along both paths I and II arise from *density* differences whereas the dynamical component results from *wave function* differences. This idea was first

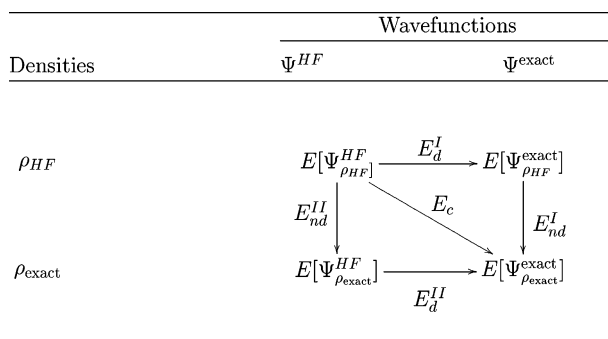


Figure 2. Quantum mechanical correlation energy,  $E_c$ , decomposition into dynamical and non-dynamical components along path I and path II.

advanced by Cioslowski [12] within the framework of the so-called *density-driven* formulation of density functional theory [34,35]. Next section will explain in more detail the physical meaning of the proposed scheme.

This energy decomposition allows to establish a straightforward relationship between other energy differences reported in the Literature. Thus, it follows that the non-dynamical component on path II, is

$$E_{\text{nd}}^{\text{II}} = \Delta + \Delta E_c, \quad (22)$$

where the quantity  $\Delta$ , introduced by Gross et al. [36], is

$$\Delta = E_x[\Psi^{\text{KS}}, \rho_{\text{exact}}] - E[\Psi^{\text{HF}}, \rho_{\text{HF}}] \quad (23)$$

and  $\Delta E_c$ , analyzed by Görling and Ernzerhof [37], is

$$\Delta E_c = E[\Psi^{\text{HF}}, \rho_{\text{exact}}] - E_x[\Psi^{\text{KS}}, \rho_{\text{exact}}]. \quad (24)$$

From these differences, we conclude that the density-functional correlation energy is related to the quantum-mechanical correlation energy through the difference  $\Delta$ ,

$$E_c^{\text{DFT}} = E_c - \Delta \quad (25)$$

or, by using the difference  $\Delta E_c$ ,

$$E_c^{\text{DFT}} = E_d^{\text{II}} + \Delta E_c, \quad (26)$$

which partially endorses the general view of considering  $E_c^{\text{DFT}}$  as composed from purely dynamical effects. Notice that this equation serves as a definition of  $\Delta E_c$  as the non-dynamical component of the density-functional correlation energy.

## 2.2. Physical interpretation of dynamical and non-dynamical correlation energy decomposition

The energy functional  $E[\Psi^\rho] = E[\Psi, \rho]$  can be expressed as a functional of three quantities: the density  $\rho$ , the locally-scaled 1-matrix  $D_\rho^1$  and the locally-scaled “diagonal” 2-matrix  $D_\rho^2$ , respectively. The energy, hence, becomes:

$$E[\Psi, \rho] = \frac{1}{2} \int d\mathbf{r} \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} D_\rho^1(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}'=\mathbf{r}} + \int d\mathbf{r} \rho(\mathbf{r}) v(\mathbf{r}) + \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{D_\rho^2(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (27)$$

The locally-scaled matrices  $D_\rho^1$  and  $D_\rho^2$  depend on the density  $\rho$  as well as on the initial untransformed wave function  $\Psi$ . To make this dependence explicit we use the following notation:  $D_\rho^1(\mathbf{r}_1, \mathbf{r}_2) \equiv D_\Psi^1([\rho], \mathbf{r}_1, \mathbf{r}_2)$  and  $D_\rho^2(\mathbf{r}_1, \mathbf{r}_2) \equiv D_\Psi^2([\rho], \mathbf{r}_1, \mathbf{r}_2)$ .



These transformed matrices can be written also in terms of the scaling vector  $\mathbf{f}$  as follows:

$$D_{\Psi}^1([\rho], \mathbf{r}, \mathbf{r}') = \sqrt{\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{\rho_{\Psi}(\mathbf{f})\rho_{\Psi}(\mathbf{f}')}} D_{\Psi}^1(\mathbf{f}, \mathbf{f}') \quad (28)$$

and

$$D_{\Psi}^2([\rho], \mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) = \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{\rho_{\Psi}(\mathbf{f}_1)\rho_{\Psi}(\mathbf{f}_2)} D_{\Psi}^2(\mathbf{f}_1, \mathbf{f}_2). \quad (29)$$

We now rewrite the 1-matrix  $D_{\Psi}^1$  in equation (28) in terms of its local and non-local components,

$$D_{\Psi}^1(\mathbf{f}, \mathbf{f}') = \rho_{\Psi}^{1/2}(\mathbf{f})\rho_{\Psi}^{1/2}(\mathbf{f}')\tilde{D}_{\Psi}^1(\mathbf{f}, \mathbf{f}'). \quad (30)$$

Similarly, we rewrite  $D_{\Psi}^2$  in equation (29) in terms of its correlation factor:

$$D_{\Psi}^2(\mathbf{f}_1, \mathbf{f}_2) = \rho_{\Psi}(\mathbf{f}_1)\rho_{\Psi}(\mathbf{f}_2) [1 + \mathbb{F}_{\Psi}^{XC}(\mathbf{f}_1, \mathbf{f}_2)]. \quad (31)$$

Introducing equations (30) and (31) into equations (28) and (29), respectively, and using these results in equation (27), we obtain the following energy functional:

$$\begin{aligned} E[\Psi, \rho] = & \frac{1}{8} \int d\mathbf{r} \frac{[\nabla\rho(\mathbf{r})]^2}{\rho(\mathbf{r})} + \frac{1}{2} \int d\mathbf{r} \rho(\mathbf{r}) \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \tilde{D}_{\Psi}^1(\mathbf{f}, \mathbf{f}') + \int d\mathbf{r} \rho(\mathbf{r}) v(\mathbf{r}) \\ & + \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)(1 + \mathbb{F}_{\Psi}^{XC}(\mathbf{f}_1, \mathbf{f}_2))}{|\mathbf{r}_1 - \mathbf{r}_2|}. \end{aligned} \quad (32)$$

Using equation (32), the dynamical component  $E_d^{\text{II}}$  along path II becomes (here  $\mathbf{f} \equiv \mathbf{f}(\mathbf{r})$ ,  $\Psi^{\text{HF}} \equiv \text{HF}$  and  $\Psi^{\text{exact}} \equiv \text{ex}$ ):

$$\begin{aligned} E_d^{\text{II}} = & E[\Psi^{\text{ex}}, \rho_{\text{ex}}] - E[\Psi^{\text{HF}}, \rho_{\text{ex}}] \\ = & \frac{1}{2} \int d\mathbf{r} \rho_{\text{ex}}(\mathbf{r}) \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} [\tilde{D}_{\text{ex}}^1(\mathbf{r}, \mathbf{r}') - \tilde{D}_{\text{HF}}^1(\mathbf{f}, \mathbf{f}')] \Big|_{\mathbf{r}'=\mathbf{r}} \\ & + \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho_{\text{ex}}(\mathbf{r}_1)\rho_{\text{ex}}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \times [\mathbb{F}_{\text{ex}}^{XC}(\mathbf{r}_1, \mathbf{r}_2) - \mathbb{F}_{\text{HF}}^X(\mathbf{f}_1, \mathbf{f}_2)], \end{aligned} \quad (33)$$

where the terms that depend on the one-particle density cancel out. An analogous expression for  $E_d^{\text{I}}$  readily follows replacing  $\rho_{\text{ex}}$  by  $\rho_{\text{HF}}$  and using the corresponding transformed density matrices.

The energy for the non-dynamical component  $E_{\text{nd}}^{\text{II}}$  is

$$\begin{aligned}
E_{\text{nd}}^{\text{II}} &= E[\Psi^{\text{HF}}, \rho_{\text{ex}}] - E[\Psi^{\text{HF}}, \rho_{\text{HF}}] \\
&= \frac{1}{8} \int d\mathbf{r} \left[ \frac{[\nabla \rho_{\text{ex}}(\mathbf{r})]^2}{\rho_{\text{ex}}(\mathbf{r})} - \frac{[\nabla \rho_{\text{HF}}(\mathbf{r})]^2}{\rho_{\text{HF}}(\mathbf{r})} \right] \\
&\quad + \frac{1}{2} \int d\mathbf{r} [\rho_{\text{ex}}(\mathbf{r}) \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \tilde{D}_{\text{HF}}^1(\mathbf{f}, \mathbf{f}') - \rho_{\text{HF}}(\mathbf{r}) \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \tilde{D}_{\text{HF}}^1(\mathbf{r}, \mathbf{r}')] \Big|_{\mathbf{r}'=\mathbf{r}} \\
&\quad + \int d\mathbf{r} [\rho_{\text{ex}}(\mathbf{r}) - \rho_{\text{HF}}(\mathbf{r})] v(\mathbf{r}) \\
&\quad + \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho_{\text{ex}}(\mathbf{r}_1) \rho_{\text{ex}}(\mathbf{r}_2) - \rho_{\text{HF}}(\mathbf{r}_1) \rho_{\text{HF}}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \\
&\quad + \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho_{\text{ex}}(\mathbf{r}_1) \rho_{\text{ex}}(\mathbf{r}_2) \mathbb{F}_{\text{HF}}^X(\mathbf{f}_1, \mathbf{f}_2) - \rho_{\text{HF}}(\mathbf{r}_1) \rho_{\text{HF}}(\mathbf{r}_2) \mathbb{F}_{\text{HF}}^X(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (34)
\end{aligned}$$

Now, according to the matrix formalism and its statistical interpretation within probability theory [38,39], it is well known that for a quantum mechanical system described by  $\Psi_{\rho}$  the conditional probability of finding an electron at point  $\mathbf{r}_1$  when one is known to be at  $\mathbf{r}_2$  (for simplicity we disregard spin) is given by

$$\rho^{\text{cond}}(\mathbf{r}_2|\mathbf{r}_1) = \frac{D_{\Psi}^2([\rho]; \mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)}, \quad (35)$$

which can be rewritten as

$$\rho^{\text{cond}}(\mathbf{r}_2|\mathbf{r}_1) = \rho(\mathbf{r}_2) + \rho_{\Psi}^h(\mathbf{r}_2|\mathbf{r}_1), \quad (36)$$

where the displaced charge (or hole) is defined as [39]

$$\rho_{\Psi}^h(\mathbf{r}_2|\mathbf{r}_1) = \rho(\mathbf{r}_2) \mathbb{F}_{\Psi}^{XC}(\mathbf{f}_1, \mathbf{f}_2). \quad (37)$$

Thus, we see that equation (33) can be written as

$$\begin{aligned}
E_d^{\text{II}} &= \frac{1}{2} \int d\mathbf{r} \rho_{\text{ex}}(\mathbf{r}) \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} [\tilde{D}_{\text{ex}}^1(\mathbf{r}, \mathbf{r}') - \tilde{D}_{\text{HF}}^1(\mathbf{f}, \mathbf{f}')] \Big|_{\mathbf{r}'=\mathbf{r}} \\
&\quad + \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho_{\text{ex}}(\mathbf{r}_1) [\rho_{\text{ex}}^h(\mathbf{r}_2|\mathbf{r}_1) - \rho_{\text{HF}}^h(\mathbf{r}_2|\mathbf{r}_1)]}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (38)
\end{aligned}$$

It is clear from equation (38) that  $E_d^{\text{II}}$  involves the change in displaced charge (or the change in Coulomb hole) produced by going from  $\Psi_{\rho_{\text{ex}}}^{\text{HF}}$  to  $\Psi^{\text{ex}}$ . In fact, the dynamical component appears solely as the difference between the exchange term of the HF wave function and the exchange-correlation term of the exact wave function, which is a *de facto* definition of correlation energy when one tries to describe correctly the Coulomb hole. The physical content of this difference becomes clear when the conditional density is interpreted as the distribution of

$N - 1$  electrons around a single one: in the space close to an electron the difference in distributions is due to the absence of correlation in the HF reference state.

On the other hand, the Coulomb hole is not involved in non-dynamical correlation. Thus, in equation (34) we see that there occurs a change in the displaced charge due to the change in density. For densities which are very similar, the non-dynamical component should be small. However, when the densities change quite drastically, as in a molecular dissociation process, this component will become relatively important.

### 2.3. Dynamical and non-dynamical correlation energies for the He and Be isoelectronic series

#### 2.3.1. He isoelectronic series

The proposed partitioning scheme has been applied to the analysis of the quantum-mechanical and density-functional correlation energy of the He isoelectronic series [13] and Beryllium isoelectronic series [40]. In this Section, the results for the He isoelectronic systems will be summarized.

In table 1 we list the total correlation energy values and its components for the helium isoelectronic series at the level of a Full CI wave function composed from orbitals  $[9s\ 8p\ 8d\ 8f\ 8g\ 8h\ 9i]$ . For  $Z \geq 2$ , we observe that the absolute values of  $E_{\text{nd}}^{\text{I}}$ , and  $E_{\text{nd}}^{\text{II}}$  are exactly the same. This fact can be explained resorting to expression for  $E_{\text{nd}}$  given by equation (34) where the main contribution comes from terms that depend on the density differences between  $\rho_{\text{HF}}$  and  $\rho_{\text{exact}}$  are involved, whereas the differences between the exchange and exchange-correlation factors for the generating and the transformed wave functions are assumed to be negligible.

In addition, it is also observed that as  $Z$  increases they become smaller and due to the fact that  $E_c$  remains constant they represent a negligible fraction of the total correlation energy. This implies that with increasing  $Z$  the correlation energy for a two-electron atom arises almost entirely from dynamical effects.

Table 1  
Dynamical and non-dynamical correlation energy components for the He isoelectronic series ( $\mu$ -Hartrees).

$Z$	$E_c$	$E_d^{\text{I}}$	$E_{\text{nd}}^{\text{I}}$	$E_d^{\text{II}}$	$E_{\text{nd}}^{\text{II}}$
2	-41963.4	-41899.4	-64.0	-42026.7	63.2
3	-43389.4	-43372.2	-17.2	-43406.6	17.2
4	-44134.1	-44126.4	-7.7	-44141.8	7.7
5	-44580.6	-44576.3	-4.4	-44585.0	4.4
6	-44911.9	-44909.2	-2.8	-44914.7	2.8

Also, the quadratical decrease of the total  $E_{\text{nd}}$  with increasing atomic number  $Z$  follows a linear pattern to a high degree of accuracy described by a relation of the form

$$E_{\text{nd}} = \frac{a}{Z^2} + c. \quad (39)$$

In table 2 a comparison between the quantum mechanical and density-functional correlation energies for the He series is made. For this purpose we list, in addition to  $E_c$ , the corresponding values for  $E_c^{\text{DFT}}$  and  $\Delta$ . For the two-electron atoms in the singlet spin state,  $\Delta E_c$  (equation (24)) is exactly zero due to the fact that the one-particle wave functions entering either in the HF or the Kohn–Sham determinant are the same and depend only on the exact density. As a consequence, we have  $E_d^{\text{II}} \equiv E_c^{\text{DFT}}$  (see equation (26)) namely, that the density-functional correlation energy is entirely composed from the dynamical contribution defined along path II. In addition, we observe that the non-dynamical component  $E_{\text{nd}}^{\text{II}}$  is equal to the correction  $\Delta$  introduced by Gross et al. [36] (see equation (23)).

### 2.3.2. Be isoelectronic series

The Beryllium isoelectronic sequence presents a pseudo-degeneracy in the  $2s^2-2p^2$  atomic levels which increases together with the charge  $Z$  in the sequence [41]. The consequence is that the HF state is no longer the only (single) reference state, instead, the configuration  $1s^2 2p^2$  should also be taken in account. This, in turn, gives rises to an appreciable long-range correlation effect created by placing electron in the orbitals  $2s$  and  $2p$  which have different regions in physical space. In this section, we present the results obtained by applying the partitioning scheme put forward in first section (for further details see Ref. [40]).

The analysis was carried out using CI wave functions arising from a  $[7s 4p 3d 2f 1g]$  orbital set optimized for an MCSCF wave function  $\Psi_{140}$  containing 140 configurations (30 for the K shell, 30 for the L shell and 80 for the intershell region). The total correlation energy recovered by this wave function

Table 2  
Comparison of quantum mechanical and density functional correlation energies for the He isoelectronic series ( $\mu$ -Hartrees).  $\Delta E_c$  is exactly zero for the entire series.

$Z$	$E_c$	$E_c^{\text{DFT}}$	$\Delta$	$\Delta$ ( Ref. [36])
2	-41963.4	-42026.7	63.2	63
3	-43389.4	-43406.6	17.2	
4	-44134.1	-44141.8	7.7	7
5	-44580.6	-44585.0	4.4	
6	-44911.9	-44914.7	2.8	

represents 97% of the estimated nonrelativistic limit for the beryllium atom [42], and 95–96% for the other members of the series [43,44].

In table 3 we give the obtained values for the dynamical and non-dynamical determined either by paths I or II. Notice that here, in opposition with the pattern found for the Helium series, the non-dynamical component  $E_c$ [nd I] is clearly proportional to the nuclear charge. This behavior is comparable to that observed for the total correlation energy for the Be series [41]. Note also that the numerical values for the components  $E_c$ [nd I] and  $E_c$ [nd II] do not coincide here. Clearly, as the near-degeneracy becomes notably stronger with the increase of atomic number, the ratio of the non-dynamical component to the total correlation energy increases up to more than 10% for the  $N^{3+}$  ion. This fact shows the inadequacy of the HF state as a first approximation to the exact state for these systems.

The decomposition of the residual correlation energy recovered by the FCI wave function taking the multireference wave function  $\Psi_R = c_1 1s^2 2s^2 + c_2 1s^2 2p^2$  as the reference wave function is shown in table 4. We may conclude, firstly, that the residual correlation energy  $E'_c = E_{\text{exact}} - E_R$  is independent of  $Z$ . This way, it resembles the behavior already observed in the He series. Secondly, that the magnitude of the non-dynamical component in relation to the total correlation energy is quite small and finally, in perfect analogy with the results for the He sequence, that in this partition a perfect coincidence between the non-dynamical

Table 3  
Dynamical and non-dynamical correlation energy components for the Be isoelectronic series ( $\mu$ -Hartrees).

$Z$	$E_c$	$E_d^I$	$E_{\text{nd}}^I$	$E_d^{II}$	$E_{\text{nd}}^{II}$
4	-91 272	-88 814	-2 458	-93 846	2 574
5	-107 776	-103 704	-4 072	-112 070	4 294
6	-121 739	-115 120	-6 619	-128 867	7 128
7	-134 946	-124 477	-10 472	-146 031	11 082

Table 4  
Analysis of the residual correlation energy,  $E'_c = E_{\text{exact}} - E_R$ , into the dynamical and non-dynamical components for the Be isoelectronic series ( $\mu$ -Hartrees).

$Z$	$E'_c$	$E_d^I$	$E_{\text{nd}}^I$	$E_d^{II}$	$E_{\text{nd}}^{II}$
4	-47 450	-47 393	-57	-47 506	56
5	-48 973	-48 953	-20	-48 994	21
6	-49 278	-49 263	-15	-49 293	15
7	-49 460	-49 451	-9	-48 819	9

parts determined by paths I and II is observed. Again, in this case, we may invoke as an explanation equation (34), with the proviso that in this case  $\rho_R$  is quite close to  $\rho_{\text{FCI}}$ . We observe that it follows the same inverse law previously found for the He sequence. This observation, plus the fact that the correlation energy  $E'_c$  does not depend on the atomic number, confirm the similarities of the correlation energy defined by the  $\Psi_R$  state for the Be series and the conventional correlation energy for the He sequence.

Table 5 lists the results of the analysis of the density-functional correlation energy found for the beryllium series. The Kohn–Sham orbitals were determined by the local-scaling scheme of kinetic-energy minimization proposed by Ludeña et al. [45]. The values of the dynamical correlation energy component  $E_d^{\text{II}}$  are also reported. We observe a great similarity between these values and those of  $E_c^{\text{DFT}}$ . In addition, we list the values of  $\Delta$  (equation (23)) and  $\Delta E_c$  (equation (24)). The increase of both these values with  $Z$  follows the same pattern as that observed for  $E_{\text{nd}}^{\text{I}}$  (the non-dynamical correlation calculated taking  $\Psi^{\text{HF}}$  as the reference wave function; see table 3. This pattern is reversed for the non-dynamical correlation energy  $E_{\text{nd}}^{\text{I}}$  as calculated with respect to the reference wave function  $\Psi_R$  (table 4). Here, these values are lowered by two orders of magnitude. Moreover, as stated previously, the residual correlation energy  $E'_c$  and  $E_d^{\text{I}}$  (cf. table 4) show a weak dependence on  $Z$  repeating the behavior already observed for the He isoelectronic series where the correlation energy defined with respect to a HF state presents a pure dynamical character. These facts clearly suggests that an alternative Kohn–Sham formalism, based on a multireference state may be more adequate for handling the correlation problem than the present one based on a single Kohn–Sham determinant.

### 3. Electron-pair density functions as fingerprints of long- and short-range effects

The features of the intracule and extracule densities provide insights into the details of electron–electron interactions. Although the the topology of both  $I(\mathbf{u})$  and  $E(\mathbf{R})$  are considerably more complex than that of the more familiar

Table 5  
Comparison of the energy differences obtained for the Be sequence ( $\mu$ -hartrees).

$Z$	$E_c$	$E_c^{\text{DFT}}$	$E_d^{\text{II}}$	$\Delta$	$\Delta E_c$
4	−91 272	−92 999	−93 846	1 727	847
5	−107 776	−110 386	−112 070	2 610	1 684
6	−121 739	−125 576	−128 867	3 837	3 291
7	−134 946	−139 868	−146 031	4 922	6 163

electron density  $\rho(\mathbf{r})$ , it has become possible to sort out different *classes* of electron–electron interactions and finding the regions of the intracule or extracule space to which they contribute [17, 19, 46–48]. It also allows the introduction of the concept of the *correlation cage* [23], as the domain in the space of interelectronic distance vectors contained within the sphere on whose surface the intracule density is locally maximum and encapsulates the electron–electron coalescence point. The shape and size of the correlation cage has been found to be entirely determined by the topological properties of the intracule density [23, 24], thus avoiding any references to ill-defined *uncorrelated* quantities.

### 3.1. Electron–electron counterbalance density as a criterion for identification of non-dynamical effects

Following this line we propose here the use of the electron–electron counterbalance density as an indicator of non-dynamical correlation effects (see also Ref. [49]). The electron–electron counterbalance density,  $d(0)$ , is a special case of the extracule density  $E(\mathbf{R})$ , i.e., it is the value at the origin  $\mathbf{R} = 0$ . For atomic systems, this probability density represents the probability of finding any two electrons at opposite sides with respect to the nucleus [30, 31, 50, 51]. In particular, it follows that in atoms long range effects of the electron correlation can be *measured* through the direct evaluation of this probability density, for it is clear that spatial separation between a pair of electrons introduced by correlating orbitals will be readily reflected in  $d(0)$ . Table 6 lists the set of wave functions used to explore the virtual atomic orbital space for the Be series. The orbitals in braces describe the configuration state functions (CSF) that enter in the MCSCF procedure. The FCI level corresponds to a wave function that includes correlating functions of angular symmetry up to  $f$ -type orbitals. It can be seen that only L-shell correlation is introduced in every wave function reflecting the expected fact [41] that near-degeneracy effects are properly accounted for by correlating only the  $2s^2$  electrons. Main entries I, II, and III correspond to wave functions including only one  $s$ ,  $p$ , or  $d$ -type orbitals. Entries labeled by lowercase letters conform to further correlating orbitals of different angular symmetry within each main entry. Since correlation contributions of both short and long range character are introduced in each wave function the particular values of  $d(0)$  for each wave function are affected in different ways. Table 6 shows the calculated counterbalance density  $d(0)$  values for this set of wave functions. It can be seen that the effect of  $s$ -type correlation in going from the HF state to the wave function I and  $I_a$  is to lower the HF value. Hence, the introduced radial correlation, interpreted as a *pushing* one electron from the other, decreases the probability of placing two electrons at mirror positions. Introduction of explicit angular  $p$  correlation as in the sequence  $\text{HF} \rightarrow \text{II} \rightarrow \text{II}_a$  rises the  $d(0)$  values. Adding extra  $d$ -type functions ( $I_c$  and  $\text{II}_b$ ) has a lowering effect on

Table 6

The electron–electron counterbalance density ratio with respect to wave function II<sub>a</sub>, for the Be isoelectronic series at the correlated wave functions.

WF		Be	B <sup>+</sup>	C <sup>2+</sup>	N <sup>3+</sup>	O <sup>4+</sup>	F <sup>5+</sup>	Ne <sup>6+</sup>
HF	$1s^2 2s^2$	0.99726	0.99543	0.99464	0.99409	0.99358	0.99328	0.99308
I	$1s^2\{2s, 3s\}^2$	0.99687	0.95156	0.95891	0.96391	0.96754	0.97032	0.97263
Ia	$1s^2\{2s, 3s, 4s\}^2$	0.99674	0.95129	0.95867	0.96369	0.96735	0.97015	0.97248
Ib	$1s^2\{2s, 3s, 2p\}^2$	0.99967	0.99960	0.99962	0.99962	0.97559	0.99964	0.99967
Ic	$1s^2\{2s, 3s, 3d\}^2$	0.99667	0.99439	0.99398	0.99300	0.99258	0.99231	0.99229
II	$1s^2\{2s, 2p\}^2$	0.99995	0.99996	0.99999	0.99999	0.99998	0.99998	0.99999
IIa	$1s^2\{2s, 2p, 3p\}^2$	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
IIb	$1s^2\{2s, 2p, 3d\}^2$	0.99975	0.99960	0.99966	0.99963	0.99966	0.99964	0.99978
III	$1s^2\{2s, 3d\}^2$	0.99688	0.99478	0.99404	0.99348	0.99306	0.99278	0.99274
IV	$1s^2\{2s, 3s, 2p, 3d\}^2$	0.99949	0.99924	0.99926	0.99926	0.99929	0.99929	0.99946
FCI		0.93717	0.95223	0.96162	0.96779	0.97221	0.97537	0.97830

counterbalance density values with respect to the main wave functions I and II, so that this type of correlation is similar to the one introduced by *s* orbitals. This is further confirmed by comparison of the values yielded by wave functions I and III. Note also that the wave function IV, although including correlation from every sort of angular symmetry used here, does not show a larger  $d(0)$  value than the “best” entry represented by wave function II<sub>a</sub>. All these results are valid for each member of the isoelectronic sequence. In general, it can be concluded that angular correlation, represented by high angular momentum correlating orbitals, has a long range (non-dynamical) character whereas radial correlation exhibits short range (dynamical) nature due to its low angular momentum and intrashell orbitals. Thus, a maximum  $d(0)$  value can be used as a criterion to select a wave function that would include the maximum non-dynamical correlation.

This criterion can also be used to understand the non-dynamical correlation effects arising from the dissociation process of the  $H_2$  molecule. In the region close to the equilibrium distance, this system can be regarded as *normal*, i.e., non-dynamical effects are negligible. As the bond is stretched, proper dissociation must be described with a multiconfigurational wave-function that includes the rising non-dynamical effects. Thus, it is expected that the electron counterbalance density should be very sensitive to the molecular dissociation.

Figure 3 depicts the values of  $d(0)$  calculated from the HF, two-orbital CSF (I), five-orbital CSF (II) and FCI wave functions using the 6-311G\*\* basis set. It is observed that, unlike the  $d(0)$  values for the HF state, the correlated wave functions present a  $d(0)$  minimum at  $R = 2.8$  a.u. This point corresponds to a perfect cylindrical charge distribution about the bond axis such that the mirror positions contribute the less to  $d(0)$ . The rising of  $d(0)$  with  $R$  is explained by



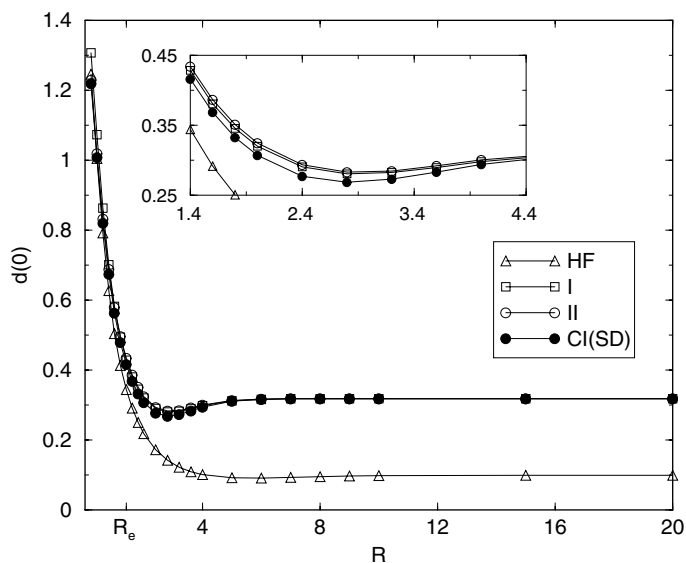


Figure 3. The electron–electron counterbalance densities,  $d(0)$ , versus the internuclear distance  $R$  for the  $H_2$  molecule (in a.u.). The wave functions were evaluated with the 6-311G\*\* basis set. The equilibrium distance  $R_e = 1.4$  a.u. is indicated on the  $R$ -axis.

the growing charge concentration in the vicinity of each atom H that eventually enhances the probability of finding a pair of electrons at opposite sides of the symmetry center. Notice that the limiting value will remain constant starting from  $R = 5$  a.u.

In figure 3 two ranges of  $R$  can be set apart. The first region extending from 0 to the equilibrium distance  $R_e = 1.4$  a.u. comprises the range where the molecule behaves as a normal system and it is expected that the HF state is a good approximation to the exact wave function. This fact is evidenced by the coincidence among all values for the electron counterbalance density of the four wave functions. Thus, up to  $R_e$ , the HF state is the simplest wave function with proper physical content in terms of the counterbalance density. The second region, ranging from  $R_e$  up to  $R = \infty$ , should be associated with the rising of near-degeneracy effects. In this region, the values for the counterbalance density for the three correlated wave functions are almost identical, whereas the HF values are clearly far from the correct trend. In this region, the wave function I is the simplest state to be chosen as the one giving the correct approximation to the electron counterbalance. The inset graph of figure 3 shows the small differences between the  $d(0)$  values in the range comprising the  $d(0)$  minimum.

Thus, the two-orbital CSF wave function should be considered as the simplest wave function that accounts for the non-dynamical effects present in this region. Notice that going to a higher level of calculation (FCI wave

function tends to lower the values of  $d(0)$ . This effect resembles the previous behavior found for the Be isoelectronic series [49], where it has been demonstrated that using highly correlated wave functions lowers the values of  $d(0)$  (cf. table 6). In the tail region beginning at  $R = 5.0$  a.u. and extending to infinity, the values of  $d(0)$  are constant and converge to the value  $1/\pi$  for all of the correlated wave functions in the set. This result agrees with the analytical value obtained for the system composed of two separated hydrogen atoms. For HF wave function the limiting value of  $d(0)$  is 0.1 which compares well with the values for a physical system that mixes spurious  $H^-$  ion-proton configurations.

Figure 4 shows the non-dynamical ( $I_I - I_{HF}$ ) and dynamical ( $I_{FCI} - I_I$ ) Coulomb electron correlation holes, along with the total Coulomb hole ( $I_{FCI} - I_{HF}$ ), for the hydrogen molecule at a nuclear separation of  $R = 1.4$  a.u. It is observed that the non-dynamical electron correlation effect dominates the Coulomb hole and, the dynamical correlation effect is substantially smaller. Notice also, that the shape of the non-dynamical hole parallels that of the total Coulomb hole, while an oscillatory behavior is seen for the dynamical electron correlation hole. The latter should be ascribed to the proper electron-electron interactions and has a *universal* sense. However, the large piece of the electron correlation, namely the non-dynamical contribution, is system dependent and reflects the incorrectness of the HF wave function as a physically sound approximation to the exact

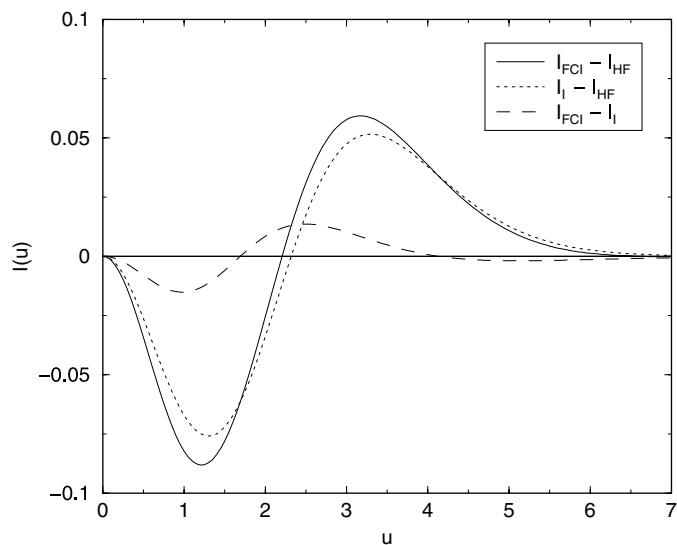


Figure 4. The electron correlation holes for the wave function I of the  $H_2$  molecule (in a.u.) at  $R=1.4$  a.u.

quantum wave function of the system. The distinct origin of these two kinds of electron correlation deserve a differentiated treatment.

#### 4. Conclusions

Electron correlation is quantity composed from a system specific, non-dynamical contribution and a non-specific, in a sense universal, dynamical contribution. The former arises from the incomplete HF description of the short-range interelectronic repulsion. The latter, is normally ascribed to the long-range correlation effects resulting from the strong interactions between the reference HF state and the closely lying pseudo-degenerate configurations.

The distinct origin of these two kinds of electron correlations deserve a differentiated treatment. However, a clear separation of the dynamical and the non-dynamical electron correlation effects is difficult. Thus, the usual Löwdin definition of the correlation energy carries both effects on the same box. Even more, the electron correlation energy, defined in this way, is not a functional of the electron density. This is quite inconvenient for progress in DFT. We have, however, based on the local-scaling transformation of the electron density, been able to find a expression for the DFT *electron correlation energy*, which is a functional of the electron density. Also, the relationship with Löwdin's electron correlation energy has been established and, a well-defined scheme to separate the contributions due to the dynamical and non-dynamical effects proposed.

This study has been complemented with the analysis of the extracuclear and intracuclear electron-pair densities. Thus, we have calculated the electron counterbalance density for a set of wave functions that partially include electron correlation energy. The changes in the electron counterbalance density have been identified with the non-dynamical (long-range) correlation contributions, since the behavior evidenced by the electron counterbalance density follows the trend observed in the balance of radial versus angular momentum correlation introduced by the correlating orbitals. Based on this criterion, a multiconfigurational wave function has been uniquely defined as such wave function that includes the maximum non-dynamical correlation. This allows for the explicit calculation of the dynamical and non-dynamical electron correlation energies and their associated intracule density distributions differences, i.e., the Coulomb holes. Our calculations demonstrate that the largest contribution to the total Coulomb hole comes from the non-dynamical electron correlation.

This suggests that there is ample room for improvement in density functional theory for efforts devoted to the proper description of systems with low lying pseudo-degenerate configurations, which are prototypical of non-dynamical electron correlation. However, we should first learn more about both types of electron correlation effects, dynamical and non-dynamical, individually, in order to devise reliable strategies to handle them efficiently.

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## References

- [1] *Methods and Techniques in Computational Chemistry, METECC-94*, ed. E. Clementi (STEF, Cagliari, 1993).
- [2] P.-O. Löwdin, *Adv. Chem. Phys.* 2 (1959) 207.
- [3] K. Ruedenberg, L.M. Cheung and S.T. Elbert, *Int. J. Quant. Chem.* 16 (1979) 1069.
- [4] B.O. Roos, *Int. J. Quant. Chem. Symp.* 14 (1980) 175.
- [5] O. Sinanoğlu, *Adv. Chem. Phys.* 6 (1964) 315.
- [6] K. Nakayama, K. Hirao and R. Lindh, *Chem. Phys. Lett.* 300 (1999) 303.
- [7] J.D. Goddard and G. Orlova, *J. Chem. Phys.* 111 (1999) 7705.
- [8] J.P. Perdew, A. Savin and K. Burke, *Phys. Rev. A* 51 (1995) 4531.
- [9] J. Gräfenstein and D. Cremer, *Chem. Phys. Lett.* 316 (2000) 569.
- [10] P.R.T. Schipper, O.V. Gritsenko, and E.J. Baerends, *J. Chem. Phys.* 111 (1999) 329.
- [11] V.A. Rassolov, *J. Chem. Phys.* 110 (1999) 3672.
- [12] J. Cioslowski, *Phys. Rev. A* 43 (1991) 1223.
- [13] E. Valderrama, E.V. Ludeña and J. Hinze, *J. Chem. Phys.* 106 (1997) 9227.
- [14] A.J. Thakkar, in: *Density Matrices and Density Functionals*, eds. R. Erdahl and V.H. Smith Jr (Reidel, Dordrecht, 1987) pp. 553–581.
- [15] R.J. Boyd and J.M. Ugalde, in: *Computational Chemistry, Part A*, ed. S. Fraga (Elsevier, Amsterdam, 1992) pp. 273–299.
- [16] E. Valderrama, J.M. Ugalde, and R.J. Boyd, in: *Advances in the Theory of Many-Electron Densities and Reduced Density Matrices*, ed. J. Cioslowski (Kluwer Academic/Plenum Publishers, Holland, 2000) pp. 231–248.
- [17] J. Cioslowski and G. Liu, *J. Chem. Phys.* 105 (1996) 8187.
- [18] C. Sarasola, L. Dominguez, M. Aguado and J.M. Ugalde, *J. Chem. Phys.* 96 (1992) 6778.
- [19] X. Fradera, M. Duran and J. Mestres, *J. Chem. Phys.* 107 (1997) 3576.
- [20] J.M. Ugalde and R.J. Boyd, *Int. J. Quant. Chem.* 29 (1986) 1.
- [21] R.J. Boyd, C. Sarasola and J.M. Ugalde, *J. Phys. B* 21 (1988) 2555.
- [22] J. Wang, A.N. Tripathi and V.H. Smith Jr, *J. Chem. Phys.* 97 (1992) 9188.
- [23] J. Cioslowski and G. Liu, *J. Chem. Phys.* 110 (1999) 1882.
- [24] J. Cioslowski, G. Liu, J. Rychlewski, W. Cancek and J. Komasa, *J. Chem. Phys.* 111 (1999) 3401.
- [25] T. Koga, *J. Chem. Phys.* 93 (1990) 5856.
- [26] T. Tsuneda, T. Suzumura and K. Hirao, *J. Chem. Phys.* 110 (1999) 10664.
- [27] P.R.T. Schipper, O.V. Gritsenko and E.J. Baerends, *Phys. Rev. A* 57 (1998) 1729.
- [28] T. Koga and H. Matsuyama, *Int. J. Quant. Chem.* 74 (1999) 455.
- [29] J.M. Ugalde and C. Sarasola, *Phys. Rev. A* 49 (1994) 3081.
- [30] T. Koga and H. Matsuyama, *J. Chem. Phys.* 107 (1997) 10062.
- [31] J.M. Mercero, J.E. Fowler, C. Sarasola and J.M. Ugalde, *Phys. Rev. A* 59 (1999) 4255.
- [32] E.V. Ludeña, R. López-Boada, V. Karasiev, R. Pino, E. Valderrama, J. Maldonado, R. Colle and J. Hinze, *Adv. Quant. Chem.* 33 (1999) 47.
- [33] E.V. Ludeña, R. López-Boada, V. Karasiev, E. Valderrama and J. Maldonado, *J. Comp. Chem.* 20 (1999) 155.
- [34] J. Cioslowski, *Phys. Rev. Lett.* 60 (1988) 2141.

- [35] E.S. Kryachko and E.V. Ludeña, *J. Chem. Phys.* 95 (1991) 9054.
- [36] E.K.U. Gross, M. Petersilka and T. Grabo, *ACS Series, Density Funct. Methods Chem.* 629 (1996) 42.
- [37] A. Görling and M. Ernzerhof, *Phys. Rev. A* 51 (1995) 4501.
- [38] R. McWeeny, *Proc. R. Soc. Lond. A* 253 (1959) 242.
- [39] R. McWeeny, *Rev. Mod. Phys.* 32 (1960) 335.
- [40] E. Valderrama, E.V. Ludeña and J. Hinze, *J. Chem. Phys.* 110 (1999) 2343.
- [41] J. Linderberg and H. Shull, *J. Mol. Spectr.* 5 (1960) 1.
- [42] O. Jitrik and C.F. Bunge, *Phys. Rev. A* 56 (1997) 2614.
- [43] E.R. Davidson, S.A. Hagstrom, S.J. Chakravorty, V.M. Umar and C. Froese-Fischer, *Phys. Rev. A* 44 (1991) 7071.
- [44] S.J. Chakravorty, S.R. Gwaltney, E.R. Davidson, F.A. Parpia and C. Froese-Fischer, *Phys. Rev. A* 47 (1993) 3649.
- [45] E.V. Ludeña, R. Lopez-Boada, J. Maldonado, T. Koga and E.S. Kryachko, *Phys. Rev. A* 48 (1993) 1937.
- [46] A.J. Thakkar and N.J. Moore, *Int. J. Quant. Chem. Symp.* 15 (1981) 393.
- [47] A.J. Thakkar, A.N. Tripathi and V.H. Smith Jr, *Int. J. Quant. Chem.* 26 (1984) 157.
- [48] X. Fradera, C. Sarasola, J.M. Ugalde and R.J. Boyd, *Chem. Phys. Lett.* 304 (1999) 393.
- [49] E. Valderrama, J.M. Mercero and J.M. Ugalde, *J. Phys. B* 34 (2001) 275.
- [50] T. Koga and H. Matsuyama, *J. Phys. B* 30 (1997) 5631.
- [51] T. Koga, *J. Chem. Phys.* 108 (1998) 2515.