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An approximate exchange-correlation hole density as a functional of the natural orbitals

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The Fermi and Coulomb holes that can be used to describe the physics of electron correlation are calculated and analysed for a number of typical cases, ranging from prototype dynamical correlation to purely nondynamical correlation. Their behaviour as a function of the position of the reference electron and of the nuclear positions is exhibited. The notion that the hole can be written as the square of a hole amplitude, which is exactly true for the exchange hole, is generalized to the total holes, including the correlation part. An Ansatz is made for an approximate yet accurate expression for the hole amplitude in terms of the natural orbitals, employing the local (at the reference position) values of the natural orbitals and the density. This expression for the hole amplitude leads to an approximate two-electron density matrix that: (a) obeys correct permutation symmetry in the electron coordinates; (b) integrates to the exact one-matrix; and (c) yields exact correlation energies in the limiting cases of predominant dynamical correlation (high Z two-electron ions) and pure nondynamical correlation (dissociated H_2).

1. Introduction

Density matrices received much attention in the early days of quantum chemistry, from the mid fifties, say, until the mid seventies. An excellent exposition of reduced density matrices is to be found in the 1976 monograph by Davidson [1], which is still a source of much of our current knowledge concerning analytical properties, symmetry aspects and physical meaning of the one-electron and two-electron density matrices. Density matrices have not had the expected impact on practical *ab initio* methods for the calculation of electronic wave functions and expectation values. By now, such calculations, going beyond Hartree–Fock (HF) in accuracy and including Coulomb correlation at some level, have become routine. The Coulomb correlation modifies the electron pair density (with respect to HF). The concept of electron pairs plays a central role in chemistry and it would therefore be natural to suppose that two-electron density matrices and the correlated pair density would have been studied extensively. Also this, however, is not the case. The number of interpretative studies of pair densities (both HF and correlated) is very small in comparison to, for example, studies of the electron density. Nevertheless, the description of electron correlation in terms of Fermi holes—describing exchange effects—and Coulomb holes—describing predominantly correlation between electrons of unlike spin—yields a clear picture of the physics of electron correlation [2]. We will use the insights obtained from such pictures to make an Ansatz for a simple yet rather accurate approximation of the two-electron density matrix in terms of the natural orbitals. The present paper is based on chapter 5 of [2].

The description of the physics of electron correlation in terms of exchange and Coulomb holes has played a more significant role in density functional theory (DFT). The practical success of DFT depends on accurate modelling of these holes. The initial success of the local density approximation (LDA) has been explained by the favourable properties of the implicitly used hole, and generalized gradient approximations (GGA) have often been proposed using arguments invoking known properties of the exact holes. Further improvement, beyond the GGAs, might come from improved modelling of the holes.

We will argue in this paper that improved modelling of holes is possible when invoking, apart from the occupied orbitals, also the virtual orbitals. First, we will analyse some effects of electron correlation using the two-electron density matrix and the related holes, in order to understand some features of electron correlation in a physical and visual manner. We will next make a contribution to accurate hole modelling by introducing the concept of a hole amplitude in which the correlated hole density is approximated by the square of an amplitude,

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analogous to the Fermi orbital concept in Hartree–Fock theory [3, 4]. We will express the hole amplitude in terms of the eigenfunctions of the one-electron density matrix, the natural orbitals. In view of the similarity in some instances between natural orbitals and Kohn–Sham orbitals [5] this provides a first step towards the extension of the well-known orbital-dependent exchange functional to an orbital-dependent exchange-correlation functional. The formulation of such a functional, and the development of a numerically stable and precise method for solving the equations for the optimized potential belonging to such an orbital-dependent exchange-correlation functional [6–8] would bring the Kohn–Sham one-electron method of density functional theory a significant step forward.

The correlation hole density can be defined by partitioning the diagonal two-particle density matrix in an uncorrelated, density-dependent part and a part describing exchange and Coulomb correlation:

$$\begin{aligned}\Gamma^{(2)}(1,2) &= \rho(1)\rho(2) + \Gamma^{(2)}_{\mathrm{XC}}(1,2)\\ &= \rho(1)\rho^{\mathrm{cond}}(2|1)\\ &= \rho(1)\{\rho(2) + \rho^{\mathrm{hole}}(2|1)\} \qquad (1)\end{aligned}$$

[coordinate 1 is a four-dimensional space-spin coordinate: $1 = r_1 s_1$; we use ρ for the diagonal part of the density matrix: $\rho(1) = \gamma(1,1)$]. The conditional density $\rho^{\mathrm{cond}}(2|1)$ is the density of the remaining $N-1$ electrons at space-spin position 2 when one electron is known to be at position r_1 with spin s_1; the hole density is the difference between the total (N-electron) density $\rho(2)$ and the conditional ($N-1$ electron) density $\rho^{\mathrm{cond}}(2|1)$. Evidently, the conditional density and hole density both depend parametrically on the position and spin of the reference electron. Note that in this article the hole density is defined as a *negative* quantity. It will integrate to minus one electron, irrespective of the position of the reference electron.

As is clear from the definition (1), the electron correlation information is concentrated in $\rho^{\mathrm{hole}}(2|1)$. In the HF approximation the hole density (also called Fermi hole or Fermi density) describes only exchange effects and is completely determined by the idempotent one-matrix. An important property of the Fermi hole from a conceptual point of view is that it can always be expressed as the square of a (normalized) orbital. This so-called Fermi orbital or Fermi amplitude, is a linear combination of the occupied HF orbitals with, for each orbital, a coefficient that depends only on local properties in the reference position r_1, namely the value of that orbital and the density ρ [3, 4]. The Fermi orbital concept has proven to be a valuable tool for the understanding of the structure of the Fermi hole. This will be illustrated in § 3 where we will analyse the Fermi hole in several atoms and molecules.

If electron correlation is introduced, e.g. in a configuration interaction (CI) calculation, the hole density is modified to include, in addition to exchange correlation, also Coulomb correlation effects. The functional dependence of the exact (exchange plus Coulomb) hole density on the diagonal one-electron density is not known, although it is a consequence of the Hohenberg–Kohn theorem that it exists. It is easier to invoke the full one-matrix, in the form of its eigenfunctions, the natural orbitals. In analogy to the Fermi amplitude concept, and its expression in terms of occupied Hartree–Fock orbitals, it is natural to ask: can one approximate the full exchange + Coulomb correlation hole in a way that is analogous to the Fermi hole in HF, by expressing it as the square of a hole amplitude? When such a hole amplitude is expanded in the set of HF orbitals, an analysis of the HF failure in weak interaction situations (e.g. H_2 dissociation) shows (see § 3) that this failure may be remedied by including virtual orbitals in the expansion. More generally, when expanding in the natural orbitals (NOs), not only the heavily occupied NOs are involved but also the weakly occupied ones. Furthermore, local properties of the system, such as the electron density and the amplitude of the NOs at the reference position enter the expression for the coefficient. The weakly occupied NOs are also more suitable for this expansion than virtual HF orbitals since they lack the diffuse nature of the latter.

It will be shown in this article that such an approximation is indeed possible and that it works remarkably well in many atoms and molecules, both in cases where the correlation is predominantly of dynamical type but also in systems with a large nondynamical (or molecular) correlation error. From a one-matrix functional [9–24] point of view the approximation is interesting because the correlated two-matrix is approximated entirely in terms of natural orbitals and occupation numbers.

The outline of this article is as follows. In § 2 we will define the correlation hole density and we will discuss the so-called Levy-Lieb partitioning of the two-matrix [25]. In this partitioning a correlated hole density is defined without reference to Hartree–Fock by constructing a HF-like ‘exchange-only’ part, making use of the correlated one-electron matrix. In § 3 we will discuss the structure of correlation holes by analysing Fermi and Coulomb holes in several two-electron and many-electron atoms and molecules. We refer to [26] for a more detailed discussion of Fermi and Coulomb holes. The usefulness of the Fermi orbital as an analysis tool will be discussed and it will be shown how the hole density for correlated two-electron systems can be approximated in terms of natural orbitals and occupation numbers by expressing the hole as the square of an amplitude, analogous to the Fermi orbital in Hartree–Fock. In § 4 the same expression for the hole amplitude is derived for general many-electron systems. The accuracy of the hole amplitude approximation is tested by comparing with the results of CI calculations on a number of two-electron and many-electron atoms and molecules. Finally, the conclusions are summarized in § 5.

2. The correlation hole and the Levy-Lieb partitioning of the two-matrix

The two-particle density matrix is the basic quantity that we will use for the study of electron correlation:

$$\Gamma^{(2)}(1,2;1',2') = N(N-1)\int \Psi(1,2,3\cdots N) \times \Psi^*(1',2',3\cdots N)\,\mathrm{d}3\cdots\mathrm{d}N. \quad (2)$$

The normalization to $N(N-1)$ is convenient for practical purposes; the number of unique electron pairs is, of course, equal to $N(N-1)/2$. The diagonal two-density or pair probability, $\Gamma^{(2)}(1,2) = \Gamma^{(2)}(1,2;1,2)$, can be interpreted as the probability that two electrons are simultaneously at positions r_1 and r_2 with spins s_1 and s_2 respectively.

The one-particle density matrix, normalized to N electrons, is given by

$$\gamma(1,1') = \frac{1}{N-1}\int \Gamma^{(2)}(1,2;1',2')\big|_{2'=2}\,\mathrm{d}2. \quad (3)$$

The one-matrix is usually expressed in natural form,

$$\gamma(1,1') = \sum_i \eta_i \chi_i(1)\chi_i^*(1'). \quad (4)$$

The χ_i are called the natural spin orbitals (NSOs) and the η_i the natural spin orbital occupation numbers. The diagonal one-density, $\rho(1) = \gamma(1,1)$, can be interpreted as the probability that an electron is at position r_1 with spin s_1.

The diagonal two-density $\Gamma^{(2)}(1,2)$ can be partitioned in an uncorrelated density dependent part and a part that describes the correlation of the electrons due to exchange and Coulomb interaction:

$$\Gamma^{(2)}(1,2) = \rho(1)\rho(2) + \Gamma^{(2)}_{\mathrm{XC}}(1,2). \quad (5)$$

For the study of electron correlation, it is only necessary to analyse the (relatively small) exchange-correlation (XC) part of the two-density. In the HF approximation, $\Gamma^{(2)}_{\mathrm{XC}}(1,2)$ only contains exchange information; the exact or CI $\Gamma^{(2)}_{\mathrm{XC}}(1,2)$ will also describe Coulomb correlation between electrons of unlike spin.

2.1. *The correlation hole density*

The expressions that we will use in this article as a definition of the exchange and Coulomb hole density can be derived from the two-density $\Gamma^{(2)}(1,2)$. We will first define the conditional density and the total hole density using space-spin coordinates, and then consider the spin-integrated quantities which we will use for the actual hole modelling.

The conditional density is defined by writing $\Gamma^{(2)}(1,2)$ as a product of the probability $\rho(1)$ that one electron is at r_1 with spin s_1 times the conditional probability that another electron is at position r_2 with spin s_2:

$$\Gamma^{(2)}(1,2) = \rho(1)\rho^{\mathrm{cond}}(2|1) \Rightarrow \rho^{\mathrm{cond}}(2|1) = \frac{\Gamma^{(2)}(1,2)}{\rho(1)}. \quad (6)$$

The conditional density can be interpreted as the density of the remaining $N-1$ electrons when one electron is known to be at position r_1 (the reference position) with spin s_1.

The hole density 'around space-spin position 1' is defined in an analogous way from $\Gamma^{(2)}_{\mathrm{XC}}(1,2)$ (see equation (5)):

$$\Gamma^{(2)}_{\mathrm{XC}}(1,2) = \rho(1)\rho^{\mathrm{hole}}(2|1) \Rightarrow \rho^{\mathrm{hole}}(2|1) = \frac{\Gamma^{(2)}_{\mathrm{XC}}(1,2)}{\rho(1)}. \quad (7)$$

Making use of partitioning (5), it is clear that $\rho^{\mathrm{hole}}(2|1)$ is the difference between the $N-1$ electron density $\rho^{\mathrm{cond}}(2|1)$ and the N electron density $\rho(2) : \rho^{\mathrm{hole}}(2|1) = \rho^{\mathrm{cond}}(2|1) - \rho(2)$. The conditional and hole density integrate to $N-1$ and -1 electron respectively, irrespective of the position of the reference electron.

The exact or CI conditional density describes exchange plus Coulomb correlation effects. When we want to study pure Coulomb correlation effects, we have to subtract the exchange-only (HF) conditional density:

$$\Delta\rho^{\mathrm{cond}}(2|1) = \frac{\Gamma^{(2)\mathrm{CI}}(1,2)}{\rho^{\mathrm{CI}}(1)} - \frac{\Gamma^{(2)\mathrm{HF}}(1,2)}{\rho^{\mathrm{HF}}(1)}. \quad (8)$$

In fact, this difference is sometimes used as a definition of the Coulomb hole [26]. However, definition (8) can lead to misleading results because the HF one-density differs from the CI one-density. The CI two-matrix will therefore also contain contributions that are needed to describe the density difference $\Delta\rho(1) = \rho^{\mathrm{CI}}(1) - \rho^{\mathrm{HF}}(1)$. These contributions 'contaminate' the Coulomb correlation information of quantities like $\Delta\rho^{\mathrm{cond}}(2|1)$, which is clear if we rewrite equation (8), making use of partitioning (5), as

$$\Delta\rho^{\mathrm{cond}}(2|1) = \Delta\rho(2) + \frac{\Gamma^{(2)\mathrm{CI}}_{\mathrm{XC}}(1,2)}{\rho^{\mathrm{CI}}(1)} - \frac{\Gamma^{(2)\mathrm{HF}}_{X}(1,2)}{\rho^{\mathrm{HF}}(1)}.$$

We can, however, reduce the complications introduced by the density difference $\Delta\rho(2)$ by defining the Coulomb hole as the hole difference instead of the conditional density difference:

$$\Delta\rho^{\mathrm{hole}}(2|1) = \rho^{\mathrm{hole,CI}}(2|1) - \rho^{\mathrm{hole,HF}}(2|1) = \frac{\Gamma^{(2)\mathrm{CI}}_{\mathrm{XC}}(1,2)}{\rho^{\mathrm{CI}}(1)} - \frac{\Gamma^{(2)\mathrm{HF}}_{X}(1,2)}{\rho^{\mathrm{HF}}(1)}. \tag{9}$$

In systems where $\Delta\rho(2)$ is negligible, definitions (8) and (9) are equivalent. Definition (9) will be used for the calculations and analysis of the Coulomb holes that are discussed in § 3.

We note in passing that if we define an exchange hole from the Kohn–Sham single determinant wavefunction, $\rho^{\mathrm{Xhole,KS}}(2|1) = \Gamma^{(2)\mathrm{KS}}_{\mathrm{X}}(1,2)/\rho(1)$, the Coulomb hole definitions according to (8) and (9) are identical since $\Delta\rho(2)$ is zero in that case. Yet another definition follows when instead of $\Gamma^{(2)\mathrm{HF}}(1,2|1',2') = \gamma^{\mathrm{HF}}(1,1')\gamma^{\mathrm{HF}}(2,2') - \gamma^{\mathrm{HF}}(1,2')\gamma^{\mathrm{HF}}(2,1')$ one uses as a reference a part of the two-matrix that is obtained from the HF like expression, but with the exact one-matrix instead of the HF one-matrix: $\Gamma^{(2)}_{0}(1,2|1',2') = \gamma(1,1')\gamma(2,2') - \gamma(1,2')\gamma(2,1')$. This so-called Levy-Lieb partitioning of the two-matrix, leading to another definition of the Coulomb hole, is especially useful when we want to compare, as we will do in § 4, an approximated two-matrix with the CI two-matrix.

It is possible to simplify the above definitions to purely spatial functions by performing suitable spin integrations. The details can be found in the Appendix. One arrives at intuitively natural quantities expressing probabilities for one (or two) electrons to be at given positions, irrespective of their spin, and conditional probabilities if another electron (irrespective of its spin) is at some other given position:

$$\rho^{\mathrm{cond}}(r_2|r_1) = \frac{\Gamma^{(2)}(r_1,r_2)}{\rho(r_1)} = \rho(r_2) + \rho^{\mathrm{hole}}(r_2|r_1), \tag{10}$$

where $\rho^{\mathrm{hole}}(r_2|r_1)$ is the hole in the total density around a reference electron at position r_1, which is a weighted average of the holes in the total density (of α plus β electrons) around an electron of α spin and around an electron of β spin:

$$\rho^{\mathrm{hole}}(r_2|r_1) = \frac{\rho^{\alpha}(r_1)}{\rho(r_1)}\rho^{\mathrm{hole},\alpha+\beta|\alpha}(r_2|r_1) + \frac{\rho^{\beta}(r_1)}{\rho(r_1)}\rho^{\mathrm{hole},\alpha+\beta|\beta}(r_2|r_1). \tag{11}$$

Note that the weights, $\rho^{\alpha}(r_1)/\rho(r_1)$ and $\rho^{\beta}(r_1)/\rho(r_1)$, only depend on the densities in the reference position. Evidently, in the closed shell case $\rho^{\mathrm{hole},\alpha+\beta|\alpha}(r_2|r_1) = \rho^{\mathrm{hole},\alpha+\beta|\beta}(r_2|r_1) = \rho^{\mathrm{hole}}(r_2|r_1)$. In the case of a determinantal wavefunction, $\rho^{\mathrm{hole},\alpha+\beta|\alpha}(r_2|r_1)$ and $\rho^{\mathrm{hole},\alpha+\beta|\beta}(r_2|r_1)$, and therefore also $\rho^{\mathrm{hole}}(r_2|r_1)$, can be written exactly as the square of an orbital (see § 3). It is the purpose of this paper to show, in § 4 and § 5, how the correlated $\rho^{\mathrm{hole}}(r_2|r_1)$ can be expressed approximately as the square of an orbital.

2.2. *The Levy-Lieb partitioning of the two-matrix*

The Levy-Lieb partitioning of the two-matrix completely bypasses the HF two-matrix and defines an 'uncorrelated' or 'zeroth order' two-matrix making use of the correlated one-matrix [12] instead of the HF one-matrix. For a HF wavefunction one has

$$\Gamma^{(2)\mathrm{HF}}(1,2;1',2') = \gamma^{\mathrm{HF}}(1,1')\gamma^{\mathrm{HF}}(2,2') - \gamma^{\mathrm{HF}}(2,1')\gamma^{\mathrm{HF}}(1,2') \tag{12}$$

and for a closed shell system, where $\gamma^{\alpha\beta} = \gamma^{\beta\alpha}$ and $\gamma^{\alpha\alpha} = \gamma^{\beta\beta} = (1/2)\gamma$ the spin integrations yield

$$\Gamma^{(2)\mathrm{HF}}(r_1,r_2) = \rho^{\mathrm{HF}}(r_1)\rho^{\mathrm{HF}}(r_2) - \tfrac{1}{2}\gamma^{\mathrm{HF}}(r_2,r_1)\gamma^{\mathrm{HF}}(r_1,r_2). \tag{13}$$

It is natural to define as a zero-order two-density of a correlated wavefunction the same expression but now in terms of the true, correlated one-matrix:

$$\Gamma^{(2)}_{0}(r_1,r_2) = \rho(r_1)\rho(r_2) - \tfrac{1}{2}\gamma(r_2,r_1)\gamma(r_1,r_2). \tag{14}$$

The total correlated two-matrix can then be partitioned as

$$\Gamma^{(2)}(r_1,r_2) = \Gamma^{(2)}_{0}(r_1,r_2) + \Gamma^{(2)}_{\mathrm{Rest}}(r_1,r_2) = \rho(r_1)\rho(r_2) - \tfrac{1}{2}\gamma(r_2,r_1)\gamma(r_1,r_2) + \Gamma^{(2)}_{\mathrm{Rest}}(r_1,r_2) \tag{15}$$

and the energy as

$$E = E_0 + E_{\mathrm{Rest}} \quad \text{with} \quad E_0 = E^{(1)}[\gamma] + E^{(2)}[\Gamma^{(2)}_{0}],$$
$$E_{\mathrm{Rest}} = \tfrac{1}{2}\int \Gamma^{(2)}_{\mathrm{Rest}}(r_1,r_2)/r_{12}\,\mathrm{d}r_1\,\mathrm{d}r_2. \tag{16}$$

The one-electron energy $E^{(1)}$ is calculated from the correlated one-matrix and is exact when γ is exact; the rest energy $E_{\mathrm{Rest}} = \frac{1}{2}\int \Gamma^{(2)}_{\mathrm{Rest}}(r_1,r_2)/r_{12}\,\mathrm{d}r_1\,\mathrm{d}r_2$ is therefore only a correction for the electron repulsion energy. In this respect E_{Rest} is different from the traditional correlation energy, which is defined as $E_{\mathrm{corr}} = E - E^{\mathrm{HF}}$ and which also contains one-electron contributions (kinetic energy and electron–nucleus Coulomb interaction) associated with the density matrix difference $\gamma(1,1') -$

$\gamma^{\mathrm{HF}}(1,1')$. E_{Rest} is sometimes called 'true correlation energy' [27] or 'one-matrix correction energy' [12].

A remarkable relation was proven by Lieb [25]: $E_0 \geq E^{\mathrm{HF}}$, which implies that $|E_{\mathrm{corr}}|$ is a lower bound for $|E_{\mathrm{Rest}}|$ even if $\gamma(1,1')$ contains fractional occupation numbers. The equality only holds if $\gamma = \gamma^{\mathrm{HF}}$. In other words, minimization of E_0 by varying the orbitals and occupation numbers will lead to γ^{HF} and E^{HF}. This result strengthens the usefulness of $\Gamma_0^{(2)}(r_1,r_2)$ as an 'uncorrelated' or zeroth order reference. The 'exchange only' nature of $\Gamma_0^{(2)}(r_1,r_2)$ is corroborated by calculations on a number of atoms and molecules that show that the hole associated with $\Gamma_0^{(2)}(r_1,r_2)$ is almost indistinguishable from the HF hole for systems for which $\rho^{\mathrm{HF}} \cong \rho^{\mathrm{CI}}$ [28]. A less attractive aspect of partitioning (15) is the fact that the hole density associated with $\Gamma_0^{(2)}(r_1,r_2)$ does not integrate to one electron but (for closed shells) to $\frac{1}{2}\sum_i \eta_i^2/N \leq 1$, where the equality holds only in the case of an idempotent γ.

From a one-matrix functional point of view [12], partitioning (15) is interesting because the total exchange + Coulomb correlation part of the two-matrix (for which a direct expression in terms of the one-matrix is unknown) is partitioned in a dominating, one-matrix dependent, 'exchange only' part, $\Gamma_0^{(2)}(r_1,r_2)$, and a relatively small rest term, $\Gamma_{\mathrm{Rest}}^{(2)}(r_1,r_2)$. Some characteristics of $\Gamma_{\mathrm{Rest}}^{(2)}(r_1,r_2)$ are discussed by Levy [12]. In § 4 an approximate expression for $\Gamma_{\mathrm{Rest}}^{(2)}(r_1,r_2)$ in terms of natural orbitals and occupation numbers is derived.

3. Fermi and Coulomb hole in atoms and molecules: the hole amplitude concept

In this section we will study exchange and Coulomb correlation by analysing correlation holes in some representative two-electron and many-electron atoms and molecules. Central in this analysis will be the concept of a hole amplitude, in which the hole density is expressed as the square of an amplitude. The HF and correlated wavefunctions and holes that are discussed were calculated in an extended basis set. The Coulomb holes, defined in equation (9), were calculated from accurate multi-reference CI wavefunctions.

3.1. *Exchange or Fermi correlation*

Fermi correlation or exchange is already incorporated in the Hartree–Fock wavefunction through the antisymmetry principle. The movement of same-spin electrons is correlated; the probability for two same-spin electrons to be at the same position in space is zero. Electrons with different spins are not correlated in HF. The Hartree–Fock pair-probability, describing the correlated electron movement, is determined completely by the density matrix:

$$\Gamma^{(2)\mathrm{HF}}(r_1,r_2) = \rho^{\mathrm{HF}}(r_1)\rho^{\mathrm{HF}}(r_2) - \tfrac{1}{2}\gamma^{\mathrm{HF}}(r_1,r_2)\gamma^{\mathrm{HF}}(r_2,r_1) \tag{17}$$

with

$$\gamma(r_1,r_1') = \sum_{i=1}^{N/2} 2\varphi_i(r_1)\varphi_i^*(r_1'). \tag{18}$$

For simplicity a closed shell is assumed, accounting for the factor 1/2 in expression (17). The exchange or Fermi hole, describing the hole density around the reference electron at position r_1, is given by

$$\rho^{\mathrm{Fermi}}(r_2|r_1) = -\frac{\frac{1}{2}\gamma(r_1,r_2)\gamma(r_2,r_1)}{\rho(r_1)}. \tag{19}$$

At first sight, the Fermi hole is difficult to interpret, due to the dependency on the off-diagonal parts of the density matrix. However, if we express $\rho^{\mathrm{Fermi}}(r_1|r_2)$ in terms of the HF orbitals, by making use of the density expression (18), we find that the Fermi density can be expressed as the square of an orbital [3, 4]:

$$\rho^{\mathrm{Fermi}}(r_2|r_1) = -\left|\varphi^{\mathrm{Fermi}}(r_2|r_1)\right|^2, \text{ with}$$

$$\varphi^{\mathrm{Fermi}}(r_2|r_1) = \sum_{i=1}^{N/2} \frac{2^{1/2}\varphi_i^*(r_1)}{[\rho(r_1)]^{1/2}}\varphi_i(r_2). \tag{20}$$

The Fermi orbital concept is attractive because it allows an easy explanation of several characteristics of the hole density. For instance, it is clear from expression (20) that in a two-electron case with only one doubly occupied orbital ϕ, the Fermi orbital is equal to this orbital and is independent of the reference position: $\varphi^{\mathrm{Fermi}}(r_2|r_1) = \phi(r_2)$.

The general Fermi orbital is a linear combination of the occupied orbitals. The orbital coefficients only depend on the orbital value and density in the reference position r_1. If the HF orbitals are localized in space then at each reference position only one orbital contributes significantly to the density and the Fermi orbital is about equal to this orbital. Furthermore, the Fermi orbital does not change considerably with changing reference position as long as the reference electron does not cross the boundary between two localized orbitals. When the reference position does cross a boundary the Fermi orbital abruptly 'jumps' from one orbital shape to the other. For example, in atoms the orbitals are localized in spatial shells: the 1s in the K shell, the 2s and 2p in the L shell etc. As long as the reference electron is somewhere in the K shell the Fermi orbital will be equal to the 1s. When the reference electron crosses the K–L boundary region the Fermi orbital will change from the 1s to a linear combination of the 2s and 2p orbitals (a sp^3 hybrid orbital). This is illustrated in figure 1 where we plot, for the Krypton atom, the Fermi

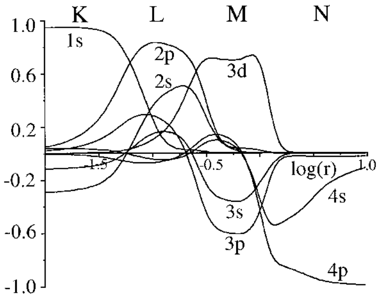


Figure 1. Fermi orbital coefficients in the krypton atom as a function of position of the reference electron.

orbital coefficients $2^{1/2}\varphi_i(r_1)/[\rho(r_1)]^{1/2}$ (the φ_i are chosen real) as a function of position of the reference electron. The atomic shell structure is clearly visible, a result that is due to the fact that the Fermi hole, equation (19), contains the off-diagonal density matrix information. (It is well known that it is much more difficult to extract the shell structure from the diagonal density ρ, which is a monotonically decreasing function in atoms [29].)

In figure 2 the Fermi hole in the N_2 molecule is plotted for four different positions of the reference electron. When the reference electron is well inside the 1s shell (figure 2 (*a*)), the 1s orbital is the only orbital that contributes significantly to the density at the reference position and the Fermi orbital is therefore equal to the 1s orbital. When the reference electron is in the bonding region on the *z* axis (figure 2 (*b*)) the Fermi orbital is about equal to the σ bond, while the Fermi orbital resembles a 'banana-bond' when the reference position is in a region where both the σ and π orbitals contribute to the density (figure 2 (*c*)).

In atoms and molecules the electrons are generally localized in shells; the size and shape of these shells

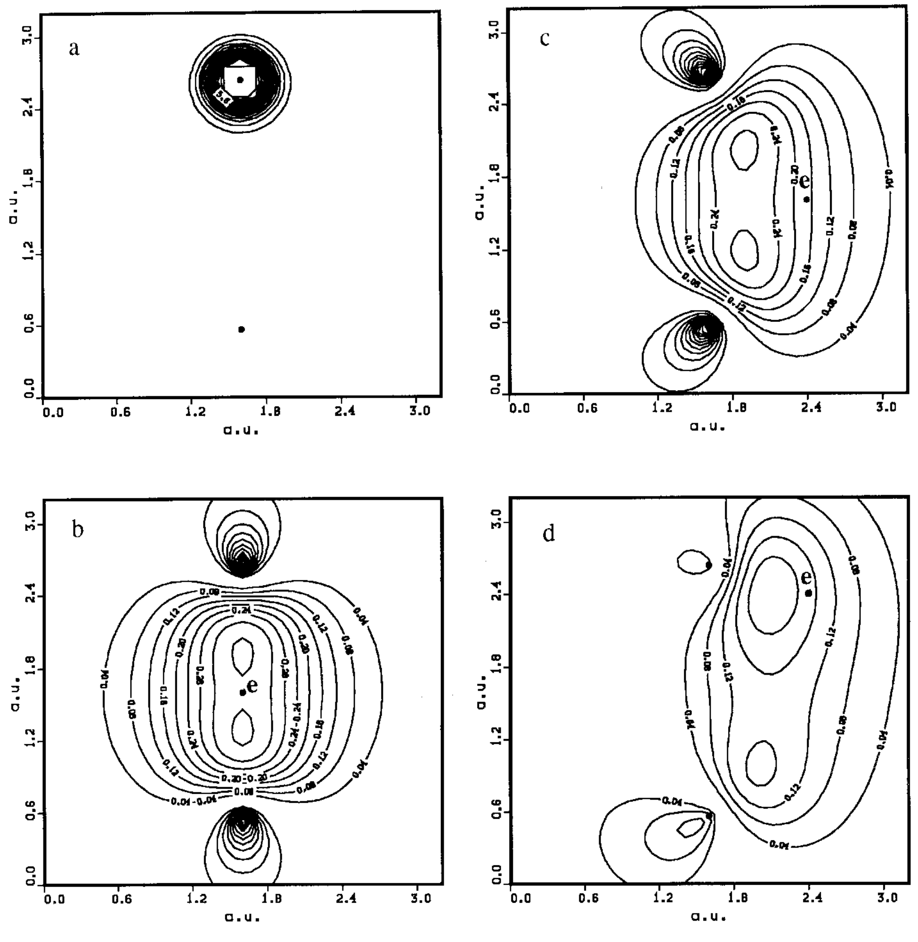


Figure 2. Fermi holes in the nitrogen molecule. The plots are in the *xz* plane. The coordinates of the nuclei are $z = -1.037$ au and $z = 1.037$ au. The reference electron is placed at the following positions: (*a*) $x = 0$, $z = 0.83$, (*b*) $x = 0$, $z = 0$, (*c*) $x = 0.8$, $z = 0$, and (*d*) $x = 0.8$, $z = 0.8$.

are determined by the positions of the nuclei. It is clear from the discussion in this section that the size and shape of the Fermi hole depend strongly on the position of the reference electron and is roughly equal to the shell that contains the reference electron. This is an important difference between actual atomic and molecular Fermi holes and approximations of the hole that are based on the electron gas.

In figure 2 (*d*) the reference position is in the bonding region near one of the nuclei. It is interesting to note that the Fermi orbital still has a significant contribution from orbitals centred on the other nucleus. This delocalization of the Fermi hole over two or more nuclei is a sign of so-called nondynamical correlation, which we will discuss in more detail in the next section.

3.2. *Strong nondynamical correlation in the dissociating electron-pair bond*

It is well known that the HF approximation fails badly for dissociation of electron pair bonds. Symmetry breaking and unphysical orbital localization are indications of a poor description at the HF level [30, 31] of weak (long) bonds. The error is usually described in terms of the ionic contributions that necessarily are contained in the simple molecular orbital (MO) wavefunction, such as $|(\sigma_g)^2|$ for H_2. It may also be described in terms of the effective one-electron potential and the exchange hole from which it arises. In figure 3 the Fermi, Coulomb and total hole in H_2 are plotted for several values of the internuclear distance R_{H-H}. In the HF approximation only one orbital, the *gerade* orbital $g = [1/(2+2S)^{1/2}] \times (s_1 + s_2)$, is doubly occupied. The Fermi orbital φ^{Fermi} (equation (20)) is therefore equal to the g orbital, irrespective of the position of the reference electron. As a result, the Fermi hole density $-|g(r_2)|^2$ is always *delocalized* over the two nuclei (see also figure 2 (*d*)). Especially at larger internuclear distance the Fermi hole is much in error, compared to the exact hole, because the exact hole is *localized* on the nucleus nearest to the reference electron, reflecting the fact that the other electron, in trying to avoid the reference electron, goes to the other nucleus.

The anomalous HF behaviour is corrected by the proper dissociation multiconfiguration self-consistent field (MCSCF) wavefunction $\Psi(1,2) = c_g|g(1)\bar{g}(2)| + c_u|u(1)\bar{u}(2)|$, where $u = [1/(2-2S)^{1/2}]$ $(s_1 - s_2)$. At infinite internuclear distance this wavefunction is exact, with coefficients equal to $c_g = 1/2^{1/2}$ and $c_u = -1/2^{1/2}$. It is interesting to note that in that case the total hole density can be expressed exactly as the square of a hole amplitude, analogous to the Fermi hole of equation (20):

$$\rho^{\text{hole}}(r_2|r_1) = -|\varphi^{\text{hole}}(r_2|r_1)|^2 \text{ with}$$

$$\varphi^{\text{hole}}(r_2|r_1) = \frac{c_g g(r_1)}{[\rho(r_1)]^{1/2}} g(r_2) - \frac{c_u u(r_1)}{[\rho(r_1)]^{1/2}} u(r_2). \qquad (21)$$

The HF error is remedied by including the antibonding u orbital in the expansion of $\varphi^{\text{hole}}(r_2|r_1)$. Note that the coefficients with which the g and u orbitals enter in the expansion are position dependent. The phases are such that when r_1 is around nucleus *a* (where s_1 is located) the hole is completely localized at *a* and has the shape $-|s_1|^2$. When the reference electron is around nucleus *b* the hole has shape $-|s_2|^2$. Yet, as in the expression for the Fermi orbital (equation (20)) the coefficients of $g(r_2)$ and $u(r_2)$ in the hole amplitude expansion (21) depend only on the orbital values and the total density in the reference position. Note that the Coulomb contribution to the hole, which describes $\alpha - \beta$ correlation and is responsible for the asymmetric spatial structure of the hole in figure 3, is about equal to the cross product $-[2c_g c_u g(r_1)u(r_1)/\rho(r_1)]g(r_2)u(r_2)$ which results from squaring the hole amplitude.

For other values of the internuclear distance, expression (21) is an approximation. The difference between this approximation and the true hole density associated with $\Psi(r_1, r_2)$ is given by (see [2]):

$$\Delta(r_2|r_1) = 4c_g^2 c_u^2 \frac{(|g(r_1)|^2 - |u(r_1)|^2)}{\rho(r_1)} (|g(r_2)|^2 - |u(r_2)|^2). \qquad (22)$$

It is clear that this difference will always be small because at long R_{H-H} the difference $|g|^2 - |u|^2$ is small, while at short R_{H-H} (e.g. $R_{H-H} = R_e$) the CI coefficient c_u is small. In figure 4 we plot the minimal basis H_2 energy for the HF function, the proper dissociation CI function and the energy calculated from the approximate two-density associated with the hole density in equation (21): $\Gamma^{(2)\text{Trial}}(r_1, r_2) = \rho(r_1)\{\rho(r_2) - |\varphi^{\text{hole}}(r_2|r_1)|^2\}$. This plot shows that, as far as the nondynamical correlation error in H_2 is concerned, the hole density can be approximated very well by the square of a hole amplitude that is a linear combination of the bonding and the antibonding orbital, i.e. of the strongly occupied natural orbitals.

3.3. *Dynamical correlation in two-electron atoms*

In systems where HF is already a good approximation, with He and two-electron ions with higher *Z* values as prototypes, the correlation (commonly called *dynamical* in this case) requires an extensive CI calculation due to the position-dependent shape of the hole and the electron cusp. To recover more than say 90% of the correlation energy, we generally need an extended basis and a large CI expansion. For example, to calcu-

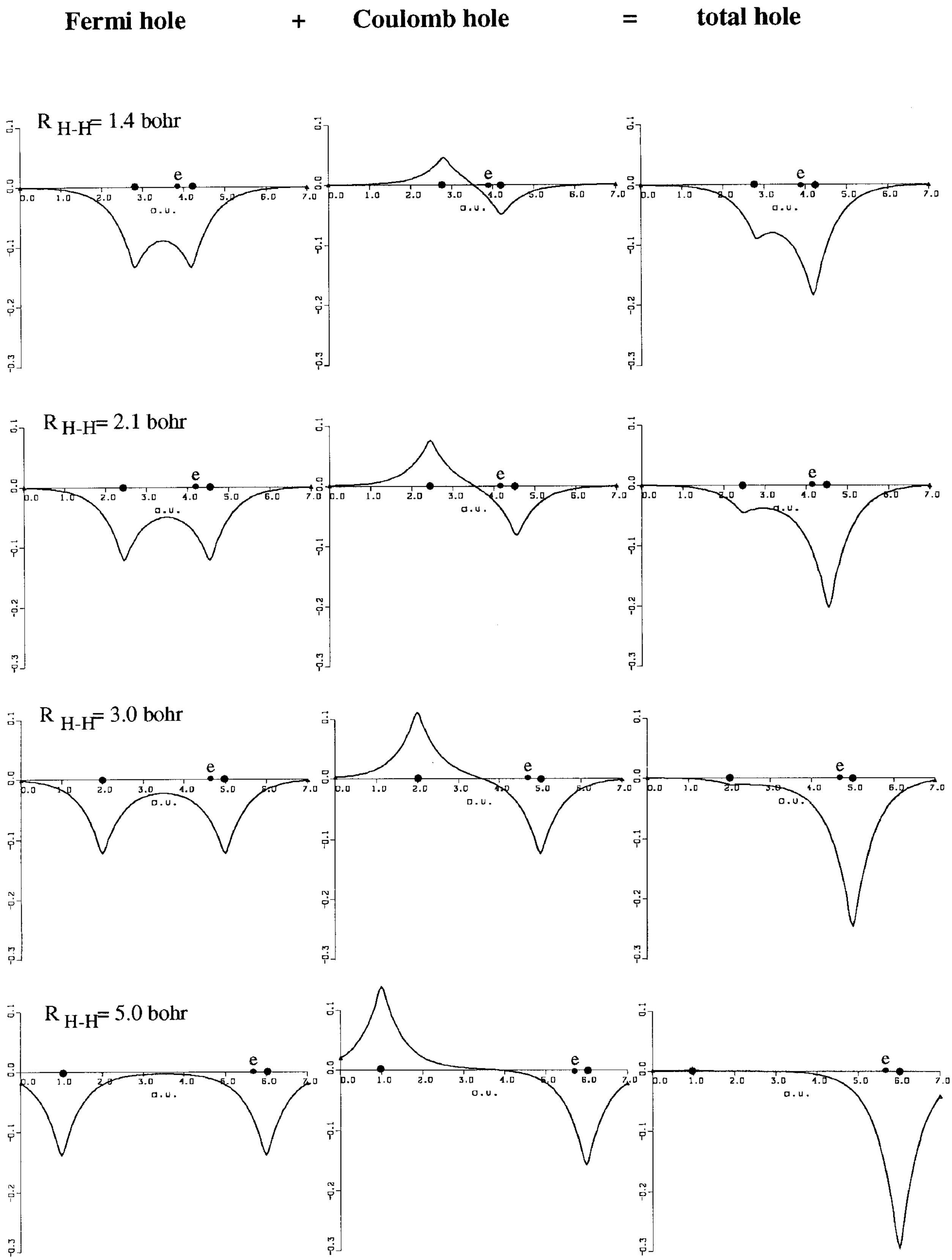


Figure 3. Fermi hole, Coulomb hole and total hole in the hydrogen molecule at various values of the internuclear distance. In all plots the reference electron is placed 0.3 bohr at the left of the right H atom.

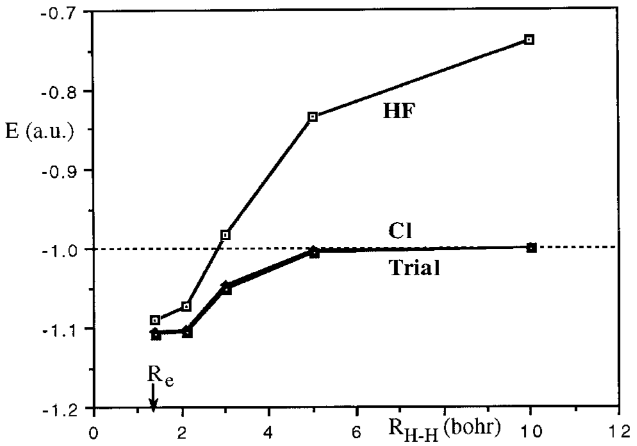


Figure 4. Minimal basis HF, CI and Trial energy for the hydrogen molecule as a function of internuclear distance.

late the binding energy of diatomic molecules like O_2 and N_2 to within a chemical accuracy of 1 kcal mol^{-1} (0.05 eV), up to f and g functions need to be included in the basis and the length of the CI expansion will be in the order of 10^7–10^8 [32].

In figure 5 the Coulomb hole in the He atom, according to definition (9), is plotted for various positions of the reference electron. It is clear that the hole is always negative around the reference electron, reflecting the fact that the interelectronic distance increases due to Coulomb correlation. These plots illustrate the two types of correlation in atoms: radial (or in–out) and angular correlation. When the reference electron is near the nucleus the correlation is of radial type and the hole is (almost) symmetric (figures 5 (*a*) and (*b*)). The probability for the second electron to be found close to the nucleus (and to the reference electron) decreases and the probability that it can be found at larger distance from the nucleus increases. At intermediate distance of the reference electron to the nucleus the correlation is a mixture of radial and angular correlation. As a result of angular correlation the probability that the second electron is found at the same side of the nucleus as the reference electron decreases while there is an increased probability for the second electron to be found at the opposite side of the nucleus. In figure 5 (*c*), at the specific distance of 0.9 bohr from the nucleus, the correlation is purely of angular type. If the reference electron is at large distance from the nucleus the correlation is again predominantly of radial type (figure 5 (*d*)). The probability for the second electron to be found close to the nucleus now increases (positive contribution to hole) because the screening effect of the reference electron has disappeared.

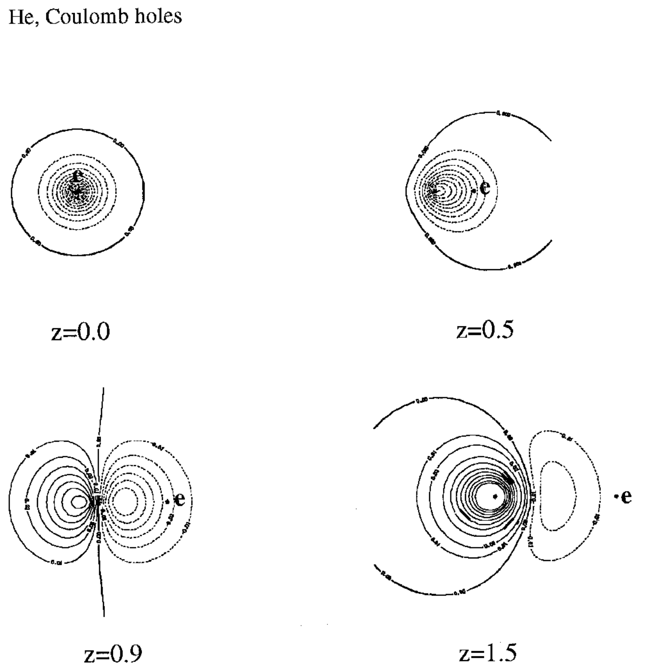


Figure 5. Coulomb holes in the He atom for several positions of the reference electron.

It is noteworthy that the Coulomb hole is almost always deepest around the nucleus and not around the reference electron. The shape and structure of the hole is further determined by the amplitude of the natural orbitals and the total density in the reference position. We can make this clear by introducing again the concept of a hole amplitude, analogous to the Fermi hole, or to the nondynamical correlation hole in H_2. In general the total hole density cannot be expressed exactly as the square of an amplitude. For two-electron systems, however, an approximate expression for the hole density in terms of natural orbitals $\{\chi_i\}$ and occupation numbers $\{\eta_i\}$ can be derived from an expression of the closed shell wave function in natural form [33]:

$$\Psi(1,2) = \sum_i c_i |\chi_i(1)\bar{\chi}_i(2)|, \quad \text{with } 2c_i^2 = \eta_i. \tag{23}$$

For He, and generally for the two-electron atoms that are isoelectronic with helium, the CI coefficients c_i are small and negative for $i \geq 2$, cf. [1, 33]. That the c_i should be negative is a direct consequence of electron correlation. It can for instance be shown [34] that double excitations from the 1s shell to the p_x, p_y and p_z orbitals, with equal coefficients c, will produce a factor $(1 + c\mathbf{r}_1 \cdot \mathbf{r}_2)$ in the wavefunction, which will lead to an increase of probability for electrons to be close together ($\mathbf{r}_1 \cdot \mathbf{r}_2$ is maximum) when c is positive. If products of two small CI coefficients are neglected, the total hole, calculated from the wavefunction expansion (23), can be approximated by the square of a hole amplitude:

$$\rho^{\text{hole}}(r_2|r_1) = -|\varphi^{\text{hole}}(r_2|r_1)|^2, \text{ with } \varphi^{\text{hole}}(r_2|r_1) = \sum_i \frac{\eta_i^{1/2}\chi_i^*(r_1)}{[\rho(r_1)]^{1/2}}\chi_i(r_2). \tag{24}$$

The hole amplitude is a linear combination of NOs with coefficients that depend on the NO values in the reference position. The overlap $\int \varphi^{\text{hole}}(r_2|r_1)\times \varphi^{\text{hole}}(r_2|r_1)^*\,dr_2 = 1$ for all reference positions r_1, in agreement with the normalization of the hole to -1 electron. In the HF approximation only the 1s term survives and φ^{hole} is equal to φ^{Fermi}. If Coulomb correlation is introduced the hole amplitude expansion is modified to include also the higher NOs. In the next section we will discuss actual calculations that will show that the hole amplitude approximation works remarkably well for two-electron atoms and will, in fact, become exact if the nuclear charge Z goes to infinity.

In figure 6 the values of the (real) hole amplitude coefficients $\eta_i^{1/2}\chi_i(r_1)/[\rho(r_1)]^{1/2}$ are plotted for the first six NOs as a function of distance from the He nucleus. It is clear from this plot that, in addition to the 1s NO, which is by far dominant, only two NOs, the 2s and 1p, contribute significantly to the hole amplitude (together with the 1s, the 2s and 1p NOs account for 85% of the total correlation energy in He [1]). By neglecting the contribution of the higher NOs we reach a simple three-term expression for the hole amplitude:

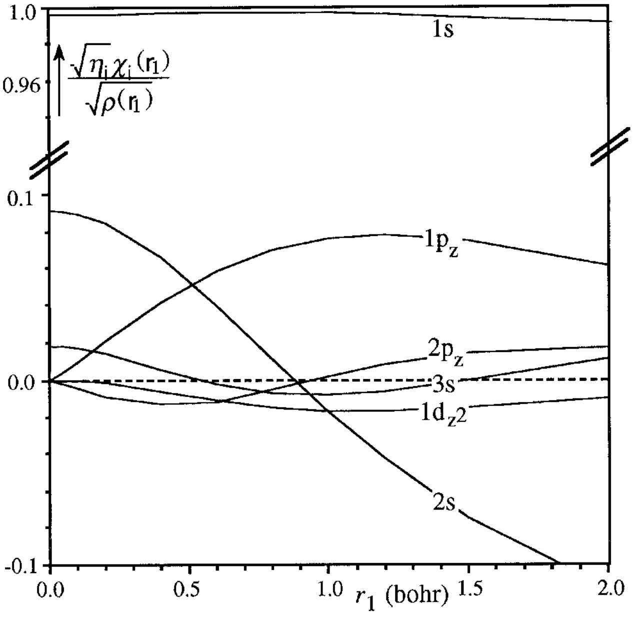


Figure 6. Composition of the hole orbital in the He atom, equation (33), as a function of position of the reference electron.

$$\varphi^{\text{hole}}(r_2|r_1) \simeq \frac{\eta_{1s}^{1/2}\chi_{1s}(r_1)}{[\rho(r_1)]^{1/2}}\chi_{1s}(r_2) + \frac{\eta_{2s}^{1/2}\chi_{2s}(r_1)}{[\rho(r_1)]^{1/2}}\chi_{2s}(r_2) + \frac{\eta_{1p}^{1/2}\chi_{1p}(r_1)}{[\rho(r_1)]^{1/2}}\chi_{1p}(r_2). \tag{25}$$

The phases of the NOs are as shown in figure 3.1a of [26], i.e. the 1s and 2s are positive at the nucleus and the 2s has a node at 0.9 bohr.

The structure of the exact Coulomb hole in He as pictured in figure 5 can be explained completely from this expression for the total (Fermi plus Coulomb) hole amplitude. The exchange part of the hole (mostly self-interaction correction) is described by the diagonal 1s^2 term (as in the HF approximation), which is the dominating contribution (only the 1s occupation η_{1s} is close to 1). The 2s and 1p terms describe the modification of the hole to include Coulomb correlation. If the reference electron is in the neighbourhood of the nucleus the hole amplitude is almost purely of s type (radial correlation), due to the fact that the orbitals of p (and higher) symmetry have a very small value in this region. The corresponding Coulomb hole, described mostly by the 1s2s cross term, is therefore nearly spherically symmetric (figures 5 (*a*) and (*b*)) and negative around the nucleus (due to the overall minus sign in equation (24)) and positive beyond 0.9 bohr. As the distance from the nucleus increases, the coefficient for the 1p NO increases and with it the contribution of the 1p orbital to the Coulomb hole; at a distance of about 0.9 au, at the node of the 2s, the 2s coefficient is zero (figure 6) and the correlation is almost purely of angular type (figure 5 (*c*)). Beyond 0.9 bohr (cf. figure 5(*d*)), the correlation becomes again of mixed angular and radial type (the latter now positive around the nucleus and negative at larger distances).

We can conclude that the dynamical correlation in this two-electron system can be described very well by an expression of the hole in terms of a hole amplitude, just as we observed before for the nondynamical correlation in the two-electron system H_2.

3.4. *Correlation in the N_2 molecule*

In figure 7 the Coulomb hole density in the N_2 molecule is plotted for several positions of the reference electron (the reference positions are the same as in the Fermi hole plots, figure 2). In a molecule we can distinguish between two regions: core and bond. When the reference electron is well inside the 1s core (figure

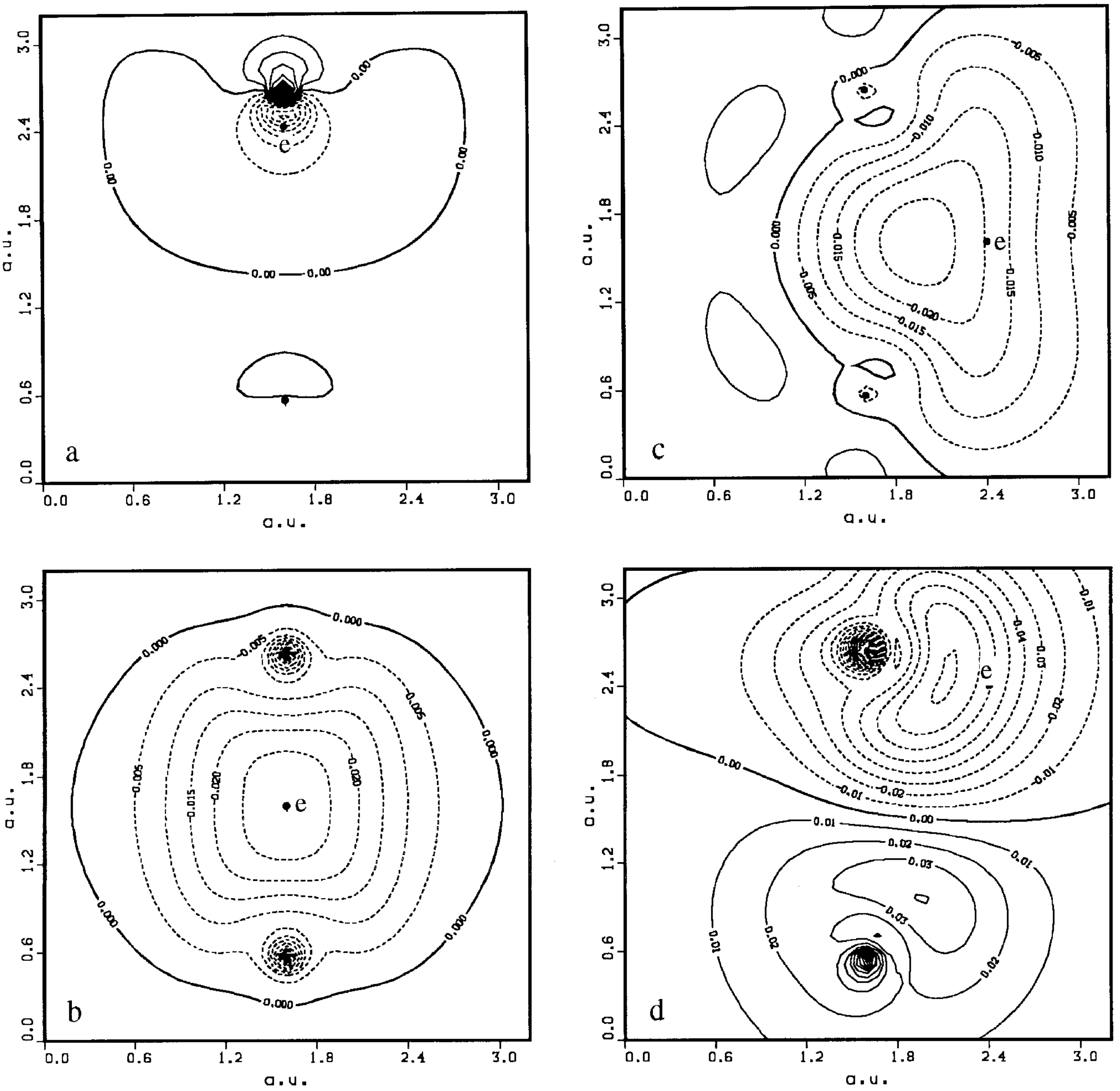


Figure 7. Coulomb holes in the nitrogen molecule. The holes are plotted in the xz plane. The nuclei are at $z = -1.037$ au and $z = 1.037$ au. The reference electron is placed at (*a*) $x = 0$, $z = 0.83$, (*b*) $x = 0$, $z = 0$, (*c*) $x = 0.8$, $z = 0$ and (*d*) $x = 0.8$, $z = 0.8$.

7 (*a*)) the hole is atomic; there are almost no contributions to the hole from other atoms in the molecule. When the reference electron is in the bonding region (figures 7 (*b*)–(*d*)) the hole is delocalized over two nuclei, just as the bonds themselves are delocalized. The size of the holes is roughly the same as the size of the Fermi holes (compare with figure 2). A noteworthy aspect of figure 7 (*d*) is that the hole is negative around the nucleus nearest to the reference electron and positive around the other nucleus. This is an example of the so-called left–right correlation and it reflects the fact that electrons, in trying to avoid the reference electron, go to the other nucleus. Left–right correlation can lead to a relatively large energy lowering when the nuclei are far

apart. The neglect of this type of nondynamical correlation by HF is the source of the well-known failure of HF to correctly describe the dissociation process.

It was shown in previous sections that the hole amplitude concept is a powerful tool in the analysis of the Fermi hole density in general and the Coulomb hole density for two-electron systems. The Coulomb holes in many-electron systems can also be explained conveniently by introducing a hole amplitude. An expression for the hole amplitude that is identical to equation (24) will be derived for many-electron systems in the next section. The accuracy of this approximation will subsequently be investigated by calculations on a number of two-electron and many-electron atoms and molecules.

4. The hole amplitude in many-electron systems

In this section we will generalize the observations made in the previous section for two-electron systems to the many-electron case. For general many-electron systems an approximate expression for the exchange-correlation hole density in terms of natural orbitals and occupation numbers can be derived by starting with the two-particle density matrix. In this derivation, the approximate exchange-correlation hole is written as the square of a hole amplitude and by the reasonable constraint that the total approximate two-matrix integrates to the correct (correlated) one-matrix, an expression for the hole amplitude is reached.

If Coulomb correlation is taken into account, the total hole density around, say, an α reference electron is modified to include, in addition to exchange, also Coulomb correlation. We will approximate this correlated hole by writing it as the square of a hole amplitude. The XC part of the approximate two-matrix describing the total hole around an α electron at position r_1 is the sum $\Gamma_{\mathrm{XC}}^{(2)\alpha\alpha}(r_1,r_2) + \Gamma_{\mathrm{XC}}^{(2)\alpha\beta}(r_1,r_2)$ (see Appendix) since the second electron may have either α or β spin. It is represented in the hole amplitude approximation by

$$\Gamma_{\mathrm{XC}}^{(2)\mathrm{Trial},\alpha+\beta|\alpha}(r_1,r_2) = -\rho^{\alpha}(r_1)\varphi^{\mathrm{hole},\alpha+\beta|\alpha}(r_2|r_1) \times \varphi^{\mathrm{hole},\alpha+\beta|\alpha}(r_2|r_1)^*. \qquad (26)$$

Since we will be dealing throughout with the *total* hole surrounding an electron with α spin (which is incidentally equal to that surrounding an electron with β spin in the closed shell systems to which we restrict ourselves), we will henceforth omit the indication α + β in the superscripts. The hole amplitude is expanded in the α natural orbitals (eigenfunctions of $\gamma^{\alpha\alpha}(r_1,r_1')$) with coefficients that depend on the reference position r_1, analogous to the expression for the Fermi orbital in equation (20):

$$\varphi^{\mathrm{hole},\alpha}(r_2|r_1) = \sum_i c_i^{\alpha}(r_1)\,\chi_i^{\alpha}(r_2). \qquad (27)$$

A physically well motivated choice for the coefficients $c_i^{\alpha}(r_1)$ in (27) can be derived, to within a phase factor, by considering two requirements that are also valid in the case of the exact $\Gamma_{\mathrm{XC}}^{(2)}$.

First, the approximate two-matrix is constrained to integrate to $N-1$ times the (correlated) one-matrix, cf. equation (A 6); $\Gamma_{\mathrm{XC}}^{(2)\mathrm{Trial},\alpha}(r_1,r_2)$ must then integrate to $-\gamma^{\alpha}(r_2)$:

$$\int \Gamma_{\mathrm{XC}}^{(2)\mathrm{Trial},\alpha}(r_1,r_2)\,\mathrm{d}r_1 = -\gamma^{\alpha}(r_2) = -\sum_i \eta_i^{\alpha}\chi_i^{\alpha}(r_2)\chi_i^{\alpha}(r_2)^* \qquad (28)$$

$\Gamma_{\mathrm{XC}}^{(2)\mathrm{Trial},\alpha}(r_1,r_2)$ defined by equations (26) and (27) will satisfy the requirement (28) for arbitrary postitions r_2 when

$$\int \rho^{\alpha}(r_1)\,c_i^{\alpha}(r_1)\,c_j^{\alpha}(r_1)^*\,\mathrm{d}r_1 = \eta_i^{\alpha}\delta_{ij}, \qquad (29)$$

which can be written as

$$\int \phi_i^{\alpha}(r_1)\,\phi_j^{\alpha}(r_1)^*\mathrm{d}r_1 = \delta_{ij} \text{ with } \phi_i^{\alpha}(r_1) \equiv \frac{[\rho^{\alpha}(r_1)]^{1/2}}{(\eta_i^{\alpha})^{1/2}}c_i^{\alpha}(r_1). \qquad (30)$$

Relation (29) is not a necessary condition on the coefficients $c_i^{\alpha}(r_1)$ since the functions $\chi_i^{\alpha}(r_2)\chi_j^{\alpha}(r_2)*$ do not constitute a complete orthonormal set. Of course (29) is a sufficient condition for (28) to hold. Equation (30) expresses that $\{\phi_i^{\alpha}\}$ is an orthonormal set of functions. We will now express $\Gamma_{\mathrm{XC}}^{(2)\mathrm{Trial},\alpha}$ in terms of the ϕ_i^{α} and use the symmetry requirement

$$\Gamma_{\mathrm{XC}}^{(2)\mathrm{Trial},\alpha}(r_1,r_2) = \Gamma_{\mathrm{XC}}^{(2)\mathrm{Trial},\alpha}(r_2,r_1), \qquad (31)$$

which leads to the result

$$\begin{aligned}\Gamma_{\mathrm{XC}}^{(2)\mathrm{Trial},\alpha}(r_1,r_2) &= -\sum_{i,j}(\eta_i^{\alpha})^{1/2}(\eta_j^{\alpha})^{1/2}\phi_i^{\alpha}(r_1) \\ &\quad \times \phi_j^{\alpha}(r_1)^*\chi_i^{\alpha}(r_2)\chi_j^{\alpha}(r_2)^* \\ &= -\sum_{i,j}(\eta_i^{\alpha})^{1/2}(\eta_j^{\alpha})^{1/2}\phi_i^{\alpha}(r_2) \\ &\quad \times \phi_j^{\alpha}(r_2)^*\chi_i^{\alpha}(r_1)\chi_j^{\alpha}(r_1)^*. \end{aligned} \qquad (32)$$

Integrating over coordinate r_1 and making use of the orthonormality of $\{\chi\}$ and $\{\phi\}$ gives

$$\sum_i \eta_i^{\alpha}\chi_i^{\alpha}(r_2)\chi_i^{\alpha}(r_2)^* = \sum_i \eta_i^{\alpha}\phi_i^{\alpha}(r_2)\phi_i^{\alpha}(r_2)^*,$$

which is satisfied when

$$\phi_i^{\alpha} = \pm\chi_i^{\alpha*} \quad \text{or} \quad c_i^{\alpha}(r_1) = \pm\frac{(\eta_i^{\alpha})^{1/2}\chi_i^{\alpha}(r_1)^*}{[\rho^{\alpha}(r_1)]^{1/2}}.$$

So we arrive in the many-electron case at the same coefficients in the expansion of the hole amplitude in the set of NOs as we obtained in the two-electron case. With respect to the choice of sign and complex phase we note that the coefficients $c_i^{\alpha}(r_1)$ are equal to those in the two-electron case, equation (24), if we choose the sign to be positive for all $c_i^{\alpha}(r_1)$. This sign and the choice of complex phase also ensures that the $c_i^{\alpha}(r_1)$ reduce to the correct HF coefficients when the occupation numbers become equal to 2 and 0 and the χ_i reduce to the Hartree–Fock orbitals, see equation (20).

So we approximate the hole amplitude completely in terms of the natural orbitals and occupation numbers:

$$\varphi^{\text{hole},\alpha}(r_2|r_1) = \sum_i \frac{(\eta_i^{\alpha})^{1/2}\chi_i^{\alpha}(r_1)^*}{[\rho^{\alpha}(r_1)]^{1/2}}\chi_i^{\alpha}(r_2). \tag{33}$$

In the case of a closed shell, $\gamma^{\alpha} = \gamma^{\beta} = \frac{1}{2}\gamma = \frac{1}{2}\sum_i \eta_i\chi_i \times (r_1)\chi_i(r_1')^*$ and there is no difference between the total hole around an α or a β electron:

$$\varphi^{\text{hole}}(r_2|r_1) = \sum_i \frac{\eta_i^{1/2}\chi_i(r_1)^*}{[\rho(r_1)]^{1/2}}\chi_i(r_2). \tag{34}$$

Making use of equation (34), the approximate two-matrix can be expressed in terms of natural orbitals and occupation numbers as follows

$$\Gamma^{(2)\text{Trial}}(r_1,r_2) = \gamma(r_1)\gamma(r_2) - \sum_{i,j}\eta_i^{1/2}\eta_j^{1/2}\chi_i(r_1)^* \times \chi_i(r_2)\chi_j(r_1)\chi_j(r_2)^*. \tag{35}$$

$\Gamma^{(2)\text{Trial}}$ has the attractive properties that it integrates to the original (correlated) one-matrix and that it reduces to the HF two-matrix if all natural occupation numbers become equal to 0 or 2. The total energy based on this approximate two-matrix can be written in terms of the familiar Coulomb and exchange integrals J and K in a form that shows how the inclusion of correlation effects modifies the familiar total energy expression of HF

$$E = \sum_i n_i\langle\chi_i| -\tfrac{1}{2}\nabla^2 + V_N|\chi_i\rangle + \tfrac{1}{2}\sum_{i,j}[n_i n_j J_{ij} - (n_i n_j)^{1/2}K_{ij}]. \tag{36}$$

We note that the $n_i^{1/2}$ weights have previously been obtained by Müller [14], who considered for $\Gamma^{(2)}_{\text{XC}}(1,2)$ the Ansatz $-\sum_{i,j} n_i^{1/2+p} n_j^{1/2-p}\chi_i(1)^*\chi_i(2)\chi_j(1)\chi_j(2)^*$ and showed that minimum deviation from the Pauli principle condition $\Gamma^{(2)}(1,2) = 0$ (which is not obeyed by the trial $\Gamma^{(2)}$) is obtained for $p = 0$. Further investigations into more general forms for the functional form of a multiplicative function $\Omega(n_i, n_j)$ for the K_{ij} in the energy expression (36) have demonstrated that the $n_i^{1/2}n_j^{1/2}$ form is inadequate in the case of the homogeneous electron gas [22, 23]. Although this may not preclude its use in molecules and atoms (see results in the next section, and see the Discussion), it certainly calls for further refinement of the natural orbital functional.

By subtracting the exchange-only part $\Gamma_0^{(2)}$ as in equation (11) we reach an approximate expression for the Coulomb correlation part of the two-matrix

$$\begin{aligned}\Gamma^{(2)\text{Trial}}_{\text{Coulomb}}(r_1,r_2) &\equiv \Gamma^{(2)\text{Trial}}_{\text{Rest}}(r_1,r_2)\\ &= \Gamma^{(2)\text{Trial}}(r_1,r_2) - \Gamma_0^{(2)}(r_1,r_2)\\ &= \sum_{i,j}\left(\tfrac{1}{2}\eta_i\eta_j - \eta_i^{1/2}\eta_j^{1/2}\right)\chi_i(r_1)^*\\ &\quad\times \chi_i(r_2)\chi_j(r_1)\chi_j(r_2)^*.\end{aligned} \tag{37}$$

Evidently, the inequality $(\frac{1}{2}\eta_i\eta_j - \eta_i^{1/2}\eta_j^{1/2}) \leq 0$ always holds if the occupation numbers are in the range $0 \leq \eta_i \leq 2$. The Coulomb correlation part of the approximate two-matrix, as defined in (37), therefore always makes a negative (more stabilizing) contribution to the total electron repulsion energy. This is as it should be because, as discussed in § 2, the energy lowering associated with the exact $\Gamma^{(2)}_{\text{Rest}}$ must always be larger (more negative) than the total correlation energy. The negative coefficients in (37) also ensure that the Coulomb hole density is negative around the reference electron. In other words, Coulomb correlation reduces the probability for an electron to be in the neighbourhood of the reference electron.

In the next section we will test the hole amplitude approximation by calculations on a number of atoms and molecules.

5. Calculations

Accurate multireference CI functions and associated one- and two-particle density matrices were calculated for a number of (closed shell) two-electron and many-electron atoms and molecules. A hole amplitude $\varphi^{\text{hole}}(r_2|r_1)$ and an approximate two-matrix $\Gamma^{(2)\text{Trial}}$ were constructed from the natural orbitals and occupation numbers (equations (34) and (35)). The Lieb partitioning (11) is especially useful for comparing $\Gamma^{(2)\text{Trial}}(r_2|r_1)$ with $\Gamma^{(2)\text{CI}}(r_2|r_1)$ because both two-matrices yield the same one-matrix upon integration and therefore differ only in the rest term $\Gamma^{(2)}_{\text{Rest}}(r_1,r_2)$. This rest term can be interpreted as describing Coulomb correlation (in the HF approximation $\Gamma^{(2)}_{\text{Rest}}(r_1,r_2) = 0$). In this section we will therefore calculate and compare Coulomb holes defined as

$$\Delta\rho^{\text{hole}}(r_2|r_1) = \frac{\Gamma^{(2)}_{\text{Rest}}(r_1,r_2)}{\rho(r_1)} \tag{38}$$

for the approximate and CI two-matrices.

In the calculation of energy expectation values much (redundant) information is integrated out, for instance the electron-repulsion energy only depends on the spherically averaged exchange-correlation hole. It is thus very well possible that an approximate hole that differs significantly from the true hole is still a good approximation as far as the energy is concerned. This is, for instance, the case with the exchange hole in the local-density approximation [35]. In addition to the holes we will therefore also compare the CI and approximate hole potentials. The hole potential will be expressed as the sum of an exchange and a Coulomb hole part in the following way:

$$\begin{aligned} V^{\mathrm{hole}}(r_1) &= -\int \frac{\rho^{\mathrm{hole}}(r_2|r_1)}{r_{12}}\,\mathrm{d}r_2 \\ &= \frac{1}{\rho(r_1)}\int \frac{-\frac{1}{2}\gamma(r_1,r_2)\gamma(r_2,r_1)}{r_{12}}\mathrm{d}r_2 \\ &\quad + \frac{1}{\rho(r_1)}\int \frac{\Gamma^{(2)}_{\mathrm{Rest}}(r_1,r_2)}{r_{12}}\mathrm{d}r_2 \\ &= V^{\mathrm{hole}}_{\mathrm{X}}(r_1) + V^{\mathrm{hole}}_{\mathrm{Rest}}(r_1). \end{aligned} \tag{39}$$

It will be shown that in many cases the Coulomb hole potential $V^{\mathrm{hole}}_{\mathrm{Rest}}(1)$ and the electron repulsion energy expectation value $E_{\mathrm{Rest}} = \frac{1}{2}\int \rho(r_1) V^{\mathrm{hole}}_{\mathrm{Rest}}(r_1)\,\mathrm{d}r_1$ calculated from the approximate two-matrix closely resemble the corresponding CI potential and energy respectively, even in those cases where the approximate and CI holes differ significantly.

Table 1. Electron repulsion energy correction E_{Rest}, equation (12). for some two-electron and many-electron systems, calculated from the CI and Trial two-matrices. Energy values in eV.

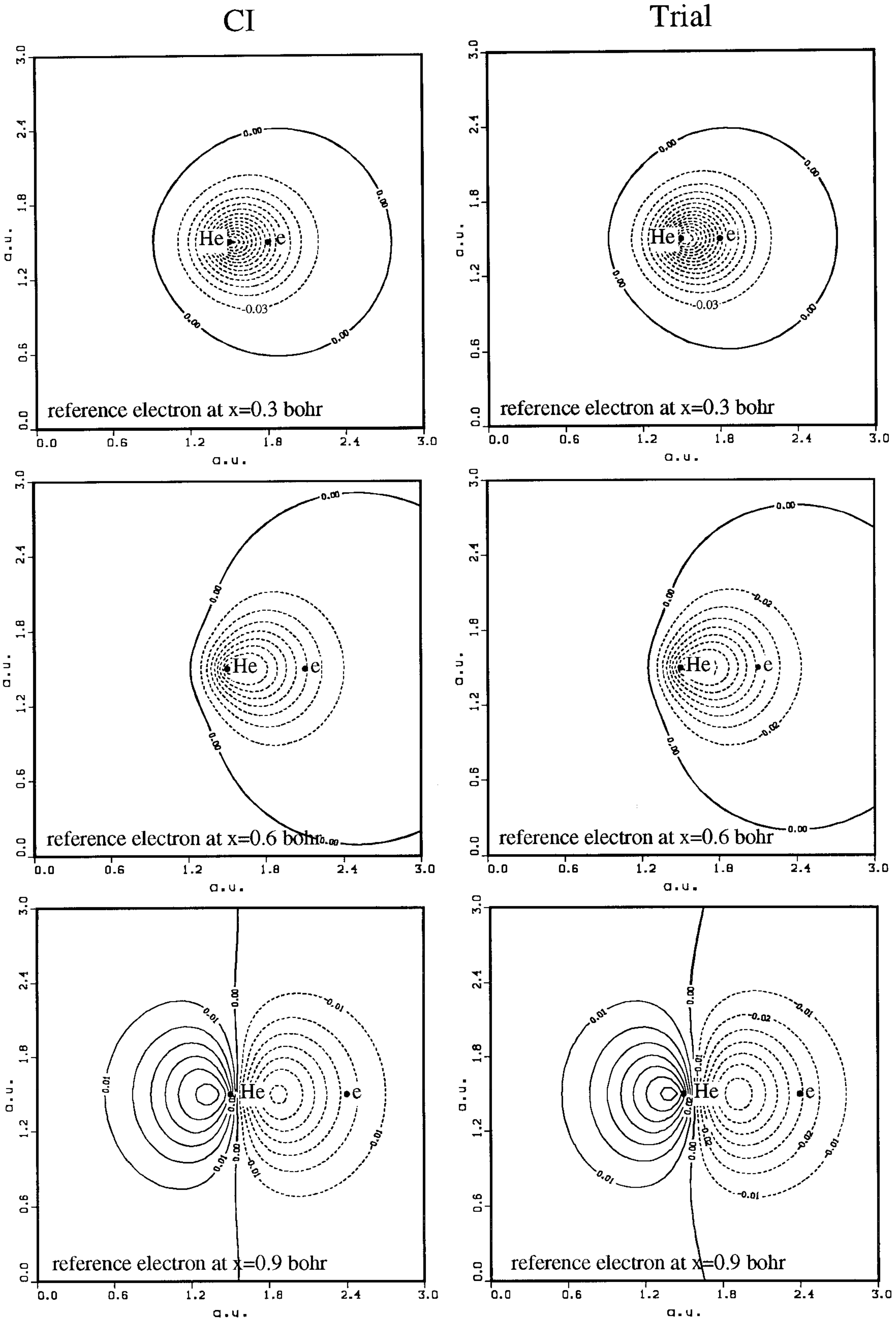
	$E^{\mathrm{CI}}_{\mathrm{Rest}}$	$E^{\mathrm{Trial}}_{\mathrm{Rest}}$	
He	−2.41	−2.62	(109%)
Be^{2+}	−2.31	−2.42	(105%)
Ne^{8+}	−2.17	−2.21	(102%)
H_2, $R_{\mathrm{H-H}} = 1.4$ au ($= R_e$)	−2.40	−2.70	(113%)
H_2, $R_{\mathrm{H-H}} = 3.0$ au	−4.77	−5.22	(109%)
H_2, $R_{\mathrm{H-H}} = 10.0$ au	−8.50	−8.51	(100%)
Be	−5.80	−6.78	(117%)
LiH	−2.33	−2.65	(114%)
Li_2	−5.78	−6.53	(113%)
H_2O	−13.7	−15.5	(113%)
Ne	−17.5	−18.4	(105%)
N_2	−19.2	−22.8	(119%)

In table 1 we list the value of E_{Rest} for several atoms and molecules. The values associated with the approximate two-matrix 'overshoot' the CI value by 0–20%. (A too large value of $E^{\mathrm{Trial}}_{\mathrm{Rest}}$ was found in all calculations, not only those listed in table 2.) Note that the error is smallest for those systems that have natural occupation numbers very close to 2 and 0 (e.g. the two-electron atoms and the Ne atom). When the deviation from 2 and 0 is larger, e.g. in the Be atom or the N_2 molecule, the error in E_{Rest} is also larger. On the other hand, the hole amplitude model is exact for H_2 at infinite internuclear distance, where the natural orbital occupations strongly differ from the HF values, becoming 1 for both the g and u orbitals. This case is traditionally considered to be a case of pure nondynamical correlation. For the case of two-electron atoms with $Z \rightarrow \infty$ the approximation also becomes exact. This is a case of predominantly dynamical correlation. The overcorrelation is probably a consequence of the too restricitive hole model we use, in particular its definite negative nature which follows from writing it as the square of hole amplitude. More refined hole modelling should remove this restriction, and in particular also differentiate according to the spin of the correlated electrons.

In figure 8 the CI and approximate Coulomb holes (equation (38)) are plotted for the He atom for several positions of the reference electron along the z axis. The approximate Coulomb hole is somewhat too deep around the reference electron which explains the fact that the energy stabilization associated with the hole is too large (table 1). The general structure of the approximate hole, however, closely resembles that of the CI hole. In figure 9 we plot the hole potential $V^{\mathrm{hole}}(r_1)$,

Table 2. Optimized occupation numbers of the σ_g and σ_u natural orbitals in the total energy using $\Gamma^{(2)\mathrm{Trial}}$. Comparison is made to two-configuration CI calculations ($(\sigma_g)^2$ and $(\sigma_u)^2$), with either the NOs or the Hartree–Fock MOs. Energies in Hartree.

		D-CI (HF basis)			D-CI (NO basis)			$\Gamma^{(2)\mathrm{Trial}}$		
$R_{\mathrm{H-H}}$	E^{HF}	E	η_g	η_u	E	η_g	η_u	E	η_g	η_u
1.4 (R_e)	−1.133	−1.134	1.999	0.001	−1.152	1.98	0.02	−1.136	1.98	0.02
2.0	−1.091	−1.094	1.99	0.01	−1.121	1.94	0.06	−1.108	1.93	0.07
3.0	−0.989	−1.015	1.89	0.11	−1.048	1.78	0.22	−1.044	1.72	0.28
5.0	−0.859	−0.972	1.33	0.67	−1.003	1.25	0.75	−1.006	1.20	0.80
10.0	−0.767	−0.973	1.01	0.99	−1.0	1.0	1.0	−1.0	1.0	1.0


CI

Trial

Figure 8. Coulomb hole in the He atom for three positions of the reference electron, calculated from the CI and Trial two-density. The position of the He nucleus, $x = 0$, is at the midpoint of the plot frame.

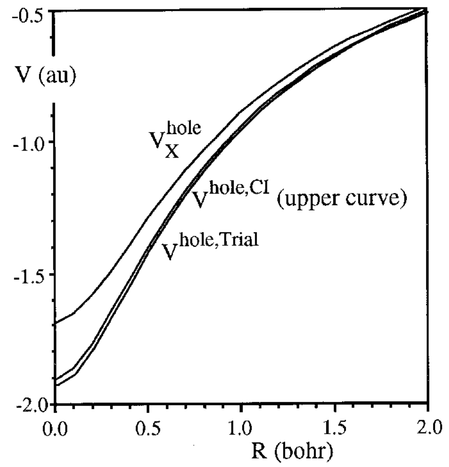


Figure 9. Hole potential, equation (39), for the He atom, calculated from CI and Trial two-matrix. The exchange only hole potential (which is about equal to the HF hole potential) is also plotted.

equation (39), calculated from the CI and approximate two-density for the He atom. The exchange only potential $V_X^{hole}(r_1)$ is also plotted. As mentioned above, the approximate hole is somewhat too deep around the reference electron; in figure 9 this is reflected in the approximate potential being somewhat too attractive, especially when the reference electron is in the neighbourhood of the nucleus. The error, however, is only small.

In table 1 and figures 10 and 11 the results of full CI calculations on H_2 are presented. The total correlation error in the H_2 molecule contains both dynamical and nondynamical components. In fact, the distinction is not sharp. We note that it is an advantage of our hole model that it is equally well applicable in cases that are traditionally considered to be of either type. At infinite internuclear distance the correlation is purely of nondynamical type and the hole orbital approximation is exact. At equilibrium internuclear distance, R_{H-H} =

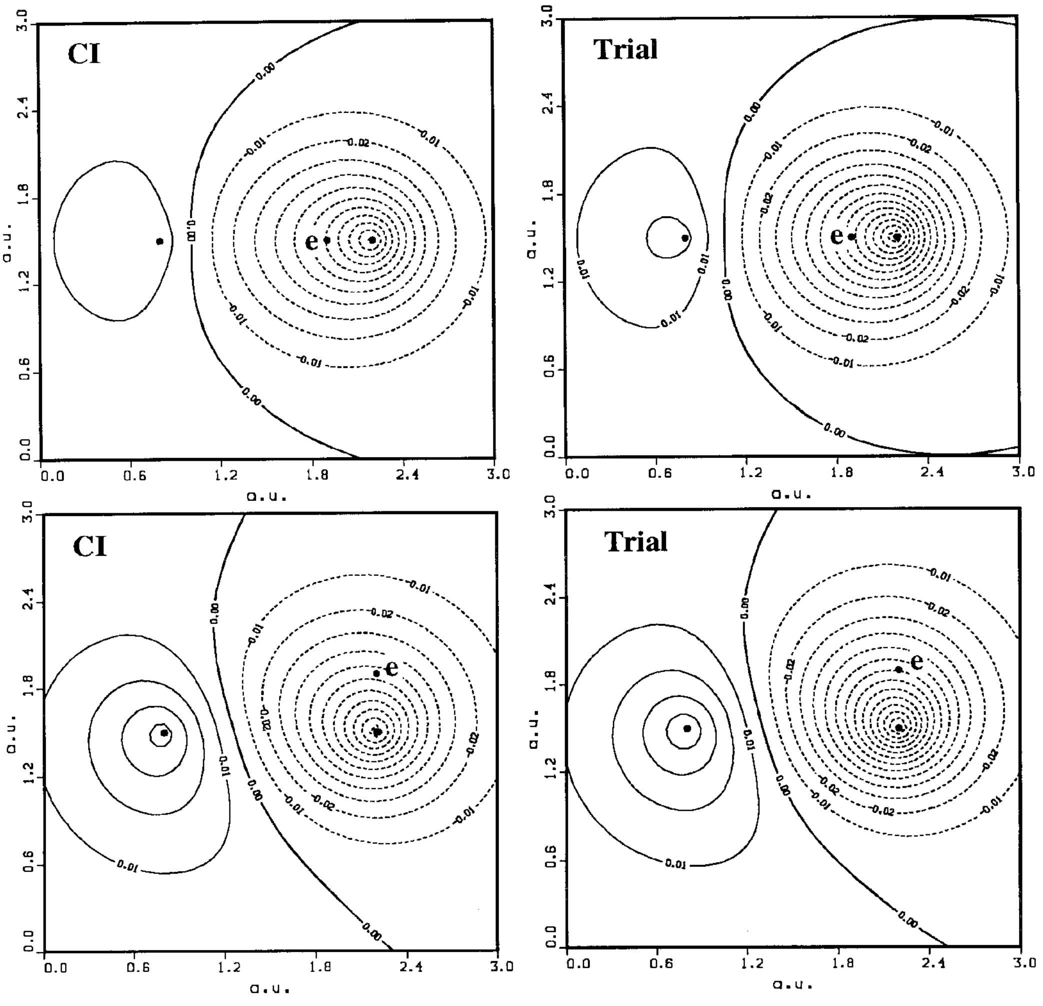


Figure 10. CI and Trial Coulomb holes in the hydrogen molecule at equilibrium internuclear distance. The reference electron is placed at the following two positions: on the bonding axis at $z = 0.4$ bohr ($z = 0$ at bond midpoint) and at $z = 0.7$ bohr, $y = 0.4$ bohr.

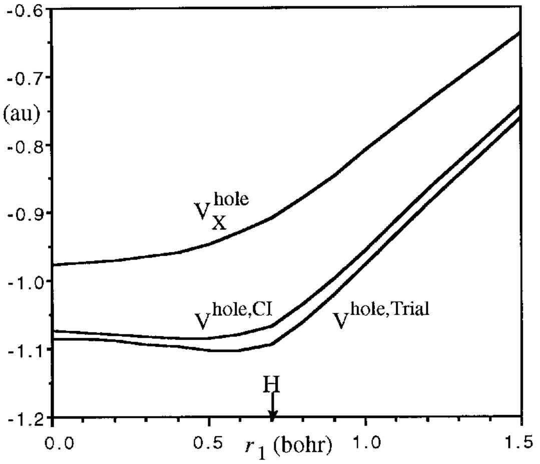


Figure 11. Hole potential, equation (39), for the hydrogen molecule at equilibrium internuclear distance (1.4 bohr), as a function of position of the reference electron along the bonding axis ($R = 0$ at midpoint of bond).

1.4 au, there will be significant angular and radial components (dynamical correlation). The error in the electron-repulsion energy is only 13% at R_e (table 1), comparable to the 9% error in He. The approximate Coulomb holes in figure 10 and the hole potential in figure 11 closely resemble the corresponding CI holes with respect to potential.

We have until now used the natural orbital occupation numbers that result from the CI calculations. It is also possible to optimize the occupation numbers so that a minimum total energy would be obtained while using $\Gamma^{(2){\rm Trial}}$. The orbitals do not suffer from the diffuseness that characterizes the HF orbitals since the one-electron equations for the orbitals contain $V^{\rm hole}(r_1)$ as the exchange-correlation potential. In order to show the behaviour of the resulting occupation numbers we give the results of such a calculation in table 2. The optimization has been limited to a two-orbital space, just the σ_g and the σ_u orbitals and a comparison is made to a simple two-orbital CI (configurations $(\sigma_g)^2$ and $(\sigma_u)^2$) with either the Hartree–Fock σ_g and σ_u orbitals or the σ_g and σ_u natural orbitals. In these CI calculations the occupation numbers result from the diagonalization of the calculated density matrix. The important point to note is that the optimized occupation numbers with the trial two-matrix are close to the natural orbital occupation numbers from the CI in the NO basis. In particular the large change from the (almost) 2–0 distribution over σ_g and σ_u at R_e to the 1.0–1.0 distribution at $R \to \infty$ is faithfully reproduced. The CI in the HF basis gives occupation numbers that show qualitatively the same behaviour but they 'lag behind' somewhat due to the extremely diffuse character of the Hartree–Fock σ_u orbital [26], making it less effective in the two-configuration CI. We note that Goedecker and Umrigar [36] have taken the $n_i^{1/2}n_j^{1/2}$ Ansatz for the XC hole term of ref [2] and have applied it in a careful optimization of orbitals and occupation numbers for a number of light atoms (He, H$^-$, Li, Be, C, Ne) with very good results.

As an example of a many-electron system we plot in figures 12 and 13 the holes and hole potential for the neon atom. Qualitatively the approximate Coulomb hole is correct (negative around the reference electron). However, the hole is too deep in the neighbourhood of the reference electron. This error can be traced to the fact that the approximate hole density is constructed exclusively from natural orbitals that have a non-zero value in the reference position. In the CI hole these orbitals will contribute less, while there are also contributions from orbitals that are zero in the reference position (e.g. due to a nodal plane).

6. Discussion

In this paper we have studied Fermi and Coulomb holes with the purpose to get a better understanding of electron correlation (see also [26]). In atoms and molecules the shape and structure of the correlation holes are strongly determined by the type and position of the nuclei. For instance, the hole maxima are almost always around the nuclei and not around the reference electron. This is an important difference between correlation holes in atoms and molecules and approximate holes that are based on the electron gas. It must therefore be judged extremely difficult to extract all the information necessary to obtain a good value for the exchange-correlation energy density at a given point from only the density and (higher) derivatives of the density at that point. In this respect it is gratifying that the generalized gradient approximations of DFT, which only use this local information, are attaining the accuracy that they, as a matter of fact, do attain. However, the dominating influence of the nuclear position on the shape and extent of the exchange and correlation holes argues very strongly in favour of schemes that use for the energy density at a point 'nonlocal' information, such as positions of maxima of the density (the nuclei, shell structure of the density, etc.). This can be achieved with the use of the Kohn–Sham orbitals, and atom-centred basis functions, for the description of the exchange-correlation energy density rather than basing this description on the local density and its derivatives.

The electrons in atoms and molecules move in more or less localized shells; the Fermi and the Coulomb hole have a size that is clearly related to that of the shell which contains the reference electron. The structure of the Fermi hole can be explained conveniently by expressing the hole as the square of an orbital. In this article we have extended the Fermi orbital model to include

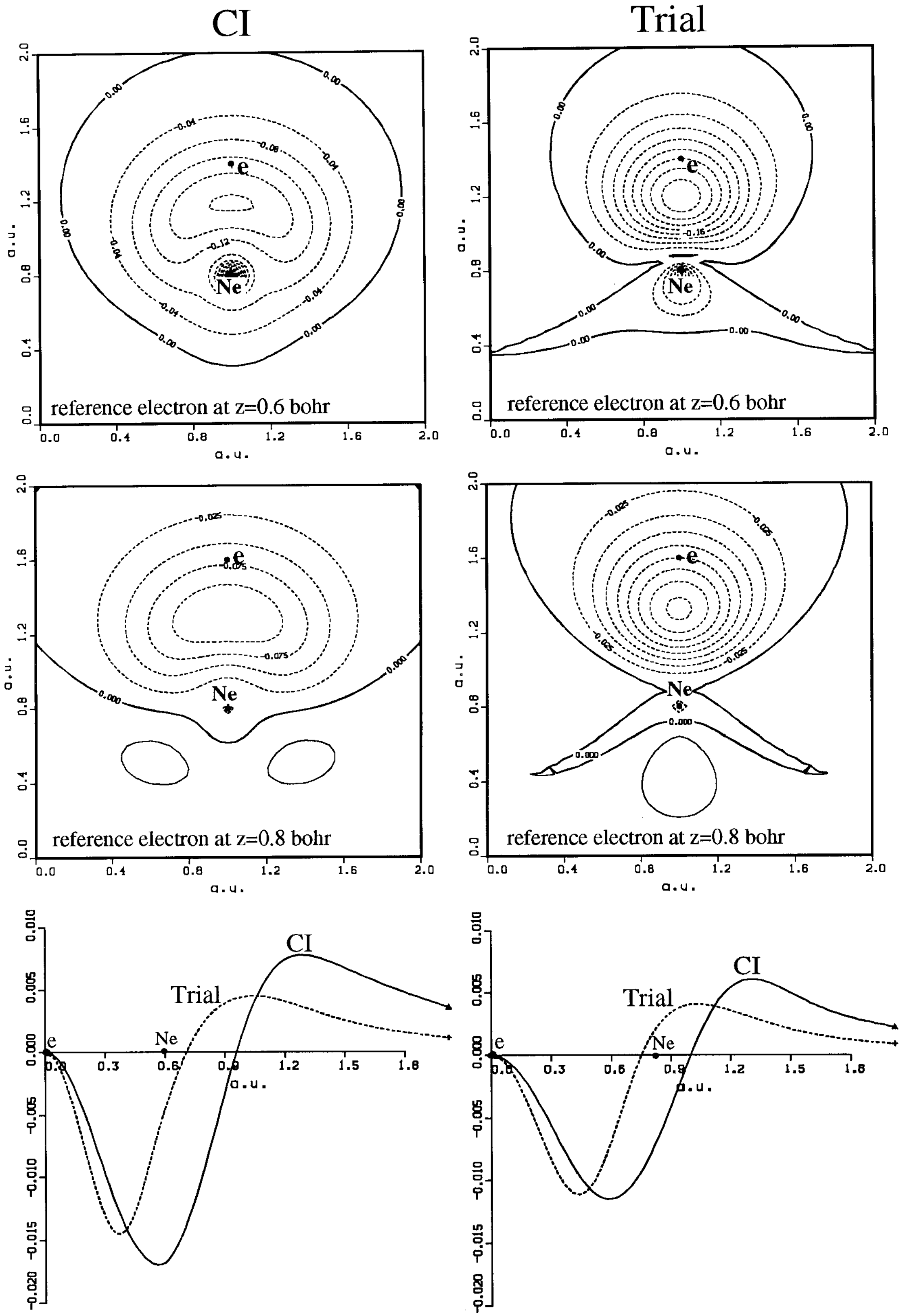


Figure 12. Coulomb holes in the Ne atom, calculated from the CI two-density and Trial two-density, for two different positions of the reference electron: $z = 0.6$ bohr and $z = 0.8$ bohr. The Ne 1s is kept closed (doubly occupied) in the CI calculations. In plots 5 and 6 the spherical averaged holes are plotted (spherical averaged around reference electron).

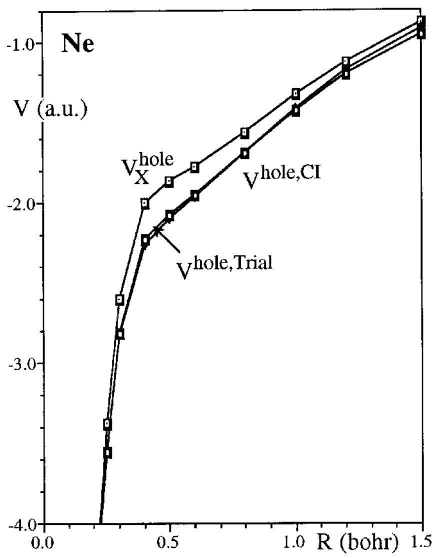


Figure 13. Hole potential for the Ne atom as a function of position of the reference electron.

also Coulomb correlation. The general hole amplitude is now a linear combination of the (occupied) natural orbitals with coefficients that depend only on the local properties of the reference electron, namely the orbital value and the total density. The natural orbitals, which we use for the hole expansion, have built in, as do the Hartree–Fock orbitals and Kohn–Sham orbitals, information on the nuclear positions, and, of course, on the spatial characteristics (atomic or molecular domain, extent) of the 'shell' the electron is in. For the coefficients still only local properties (at the reference position) need to be used.

The idea that local properties of the reference electron can be used to derive properties of the hole, combined with the fact that the complexity of the problem is greatly reduced when working with quantities that depend only on the (diagonal) density, is the basis of virtually all approximation schemes of density functional theory. In the hole amplitude model, we have started with the correlated one-matrix and we have used, in addition to the value of $\rho(r_1)$, also the value of the (natural) orbitals in the reference position; i.e. we are using both diagonal and off-diagonal information in the density matrix for the construction of an approximate hole. With the hole amplitude approximation, the (qualitative) structure of the Coulomb hole can be explained remarkably well.

The application of these ideas in a DFT context is currently being explored [37]. We then have in principle only the Kohn–Sham orbitals available, not the natural orbitals. In the case of nondynamical correlation in H_2 the prospects are good, since the Kohn–Sham orbitals have precisely the same shape as the NOs, which is not the case for the HF orbitals. At long distances already the occupied σ_g HF orbital is too diffuse, but the virtual HF σ_u orbital is inordinately diffuse (cf. figure 4.2 of [26]) and totally unsuitable for the hole amplitude expansion. In contrast, the Kohn–Sham orbitals have a perfect 1s type shape around each nucleus, due to the presence of the Coulomb hole potential in the exact Kohn–Sham potential [38, 39]. In other cases of nondynamical correlation, like the σ–π near-degeneracy case of C_2 around the equilibrium bond length, we have also observed good resemblance of Kohn–Sham and natural orbitals [5]. This means that for the weak interaction case of dissociating electron pair bonds, but also for nondynamical correlation cases in general, including transition states, the use of Kohn–Sham orbitals within the present approach is promising. The orbital dependent exchange-correlation functional that follows from the present hole model can be shown to lead to the correct Kohn–Sham potential (no screening by the other electron) around each nucleus in the dissociated H_2 molecule, and thus for the first time offers the possibility to describe this system accurately (indeed, exactly) with density-functional theory [37].

The situation may be less favourable for dynamical correlation, since the Kohn–Sham orbitals do not have the typical tight nature that characterizes the NOs. The comparison in figure 1, p. 78 of [1] of the first NOs of He with Rydberg orbitals shows the narrow character of the 2s NO, having its node at 0.9 bohr (which was important in our analysis of radial and angular types of correlation) and its maximum at ca. 1.8 bohr, while the 2s Rydberg orbital has a node at 1.5 bohr and a maximum at 4.4 bohr.

Appendix: Spin-integrated conditional and hole densities

The full two-density has in principle 16 spatial components resulting from expansion in a complete set of spin functions:

$$\Gamma^{(2)}(1,2;1',2') = \sum_{\sigma_1\sigma_2\sigma_3\sigma_4}^{\alpha,\beta} \Gamma^{\sigma_1\sigma_2\sigma_3\sigma_4}(r_1,r_2;r_1',r_2') \times \sigma_1(s_1)\sigma_2(s_2)\sigma_3^*(s_1')\sigma_4^*(s_2'). \qquad \text{(A 1)}$$

(For wavefunctions with given spin symmetry S, the number of independent spatial components M is reduced, cf. [1, 40].) After spin integration only the four spatial components for which $\sigma_1 = \sigma_3$ and $\sigma_2 = \sigma_4$ will remain

$$\begin{aligned}\Gamma^{(2)}(r_1,r_2;r_1',r_2') &= \int \mathrm{d}s_1\,\mathrm{d}s_2\,\Gamma^{(2)}(r_1s_1,r_2s_2;r_1's_1,r_2's_2)\\ &= \Gamma^{\alpha\alpha;\alpha\alpha}(r_1,r_2;r_1',r_2') + \Gamma^{\alpha\beta;\alpha\beta}(r_1,r_2;r_1',r_2')\\ &\quad + \Gamma^{\beta\alpha;\beta\alpha}(r_1,r_2;r_1',r_2') + \Gamma^{\beta\beta;\beta\beta}(r_1,r_2;r_1',r_2')\end{aligned} \qquad \text{(A 2)}$$

and the diagonal element is written as

$$\Gamma^{(2)}(r_1,r_2)=\Gamma^{\alpha\alpha}(r_1,r_2)+\Gamma^{\alpha\beta}(r_1,r_2)+\Gamma^{\beta\alpha}(r_1,r_2)+\Gamma^{\beta\beta}(r_1,r_2). \quad (\mathrm{A}\,3)$$

The diagonal spatial components have the obvious interpretation of probabilities to find two electrons simultaneously at r_1 and r_2 with the spins indicated in the superscript.

Similarly there are in principle four spatial components of the one-density, $\gamma^{\alpha\alpha}(r_1,r_1')$, $\gamma^{\alpha\beta}(r_1,r_1')$, $\gamma^{\beta\alpha}(r_1,r_1')$ and $\gamma^{\beta\beta}(r_1,r_1')$ (only two for eigenfunctions of S_z, see [1]). After spin integration we obtain for the spatial one-matrix

$$\gamma(r_1,r_1')=\int \mathrm{d}s_1\gamma(r_1s_1;r_1's_1)=\gamma^{\alpha\alpha}(r_1,r_1')+\gamma^{\beta\beta}(r_1,r_1') \quad (\mathrm{A}\,4)$$

and the diagonal element can be written, using $\rho^{\alpha}(r_1)=\gamma^{\alpha\alpha}(r_1,r_1)$ and $\rho^{\beta}(r_1)=\gamma^{\beta\beta}(r_1,r_1)$,

$$\rho(r_1)=\gamma(r_1,r_1)=\rho^{\alpha}(r_1)+\rho^{\beta}(r_1). \quad (\mathrm{A}\,5)$$

Each of the four contributions to the diagonal two-density can be further partitioned by expressing it as the sum of an uncorrelated density dependent part and a correlation part, e.g. $\Gamma^{(2)\alpha\beta}(r_1,r_2)=\rho^{\alpha}(r_1)\,\rho^{\beta}(r_2)+\Gamma^{(2)\alpha\beta}_{\mathrm{XC}}(r_1,r_2)$. The normalization for the various parts is as follows (N^{α} and N^{β} are the number of α and β electrons respectively):

$$\int \Gamma^{(2)\alpha\alpha}(r_1,r_2)\,\mathrm{d}r_2=(N^{\alpha}-1)\rho^{\alpha}(r_1),$$

$$\int \Gamma^{(2)\alpha\alpha}(r_1,r_2)\,\mathrm{d}r_1\,\mathrm{d}r_2=N^{\alpha}(N^{\alpha}-1),$$

$$\int \Gamma^{(2)\alpha\alpha}_{\mathrm{XC}}(r_1,r_2)\,\mathrm{d}r_2=-\rho^{\alpha}(r_1),$$

$$\int \Gamma^{(2)\alpha\alpha}_{\mathrm{XC}}(r_1,r_2)\,\mathrm{d}r_1\,\mathrm{d}r_2=-N^{\alpha},$$

$$\int \Gamma^{(2)\alpha\beta}(r_1,r_2)\,\mathrm{d}r_2=N^{\beta}\rho^{\alpha}(r_1),$$

$$\int \Gamma^{(2)\alpha\beta}(r_1,r_2)\,\mathrm{d}r_1\,\mathrm{d}r_2=N^{\alpha}N^{\beta},$$

$$\int \Gamma^{(2)\alpha\beta}_{\mathrm{XC}}(r_1,r_2)\,\mathrm{d}r_2=0,$$

$$\int \Gamma^{(2)\alpha\beta}_{\mathrm{XC}}(r_1,r_2)\,\mathrm{d}r_1\,\mathrm{d}r_2=0 \quad (\mathrm{A}\,6)$$

and analogously for the β–β and β–α parts.

The conditional density and the hole density for electrons described by space-spin coordinates have been defined in equations (6) and (7) respectively. We can also define spatial conditional and hole densities with each of the four contributions to the two-density. If the reference electron has α spin we get

$$\begin{aligned}\rho^{\mathrm{cond},\alpha|\alpha}(r_2|r_1)&=\frac{\Gamma^{(2)\alpha\alpha}(r_1,r_2)}{\rho^{\alpha}(r_1)}\\&=\frac{\rho^{\alpha}(r_1)\rho^{\alpha}(r_2)+\Gamma^{(2)\alpha\alpha}_{\mathrm{XC}}(r_1,r_2)}{\rho^{\alpha}(r_1)}\\&=\rho^{\alpha}(r_2)+\rho^{\mathrm{hole},\alpha|\alpha}(r_2|r_1),\\ \rho^{\mathrm{cond},\beta|\alpha}(r_2|r_1)&=\frac{\Gamma^{(2)\alpha\beta}(r_1,r_2)}{\rho^{\alpha}(r_1)}\\&=\frac{\rho^{\alpha}(r_1)\rho^{\beta}(r_2)+\Gamma^{(2)\alpha\beta}_{\mathrm{XC}}(r_1,r_2)}{\rho^{\alpha}(r_1)}\\&=\rho^{\beta}(r_2)+\rho^{\mathrm{hole},\beta|\alpha}(r_2|r_1).\end{aligned} \quad (\mathrm{A}\,7)$$

Analogous expressions hold if the reference electron has β spin. Making use of equations (A 6) it is easy to verify that the same-spin holes $\rho^{\mathrm{hole},\alpha|\alpha}$ and $\rho^{\mathrm{hole},\beta|\beta}$ (which are often called exchange holes because the antisymmetry principle is responsible for the dominating part) integrate to -1 electron while the opposite-spin or Coulomb holes $\rho^{\mathrm{hole},\alpha|\beta}$ and $\rho^{\mathrm{hole},\beta|\alpha}$ integrate to 0.

The total hole density around an electron with α spin at reference position r_1, which is the one we will try to approximate, is simply the sum of the hole in the density of electrons with α spin and the hole in the density of electrons with β spin:

$$\begin{aligned}\rho^{\mathrm{cond},\alpha+\beta|\alpha}(r_2|r_1)&=\frac{\Gamma^{(2)\alpha\alpha}(r_1,r_2)+\Gamma^{(2)\alpha\beta}(r_1,r_2)}{\rho^{\alpha}(r_1)}\\&=\frac{\rho^{\alpha}(r_1)\rho^{\alpha}(r_2)+\Gamma^{(2)\alpha\alpha}_{\mathrm{XC}}(r_1,r_2)}{\rho^{\alpha}(r_1)}\\&\quad+\frac{\rho^{\alpha}(r_1)\rho^{\beta}(r_2)+\Gamma^{(2)\alpha\beta}_{\mathrm{XC}}(r_1,r_2)}{\rho^{\alpha}(r_1)}\\&=\{\rho^{\alpha}(r_2)+\rho^{\beta}(r_2)\}\\&\quad+\{\rho^{\mathrm{hole},\alpha|\alpha}(r_2|r_1)+\rho^{\mathrm{hole},\beta|\alpha}(r_2|r_1)\}\\&=\rho(r_2)+\rho^{\mathrm{hole},\alpha+\beta|\alpha}(r_2|r_1).\end{aligned} \quad (\mathrm{A}\,8)$$

In the case of a determinantal wave function $\rho^{\mathrm{hole},\alpha+\beta|\alpha}(r_2|r_1)$ and $\rho^{\mathrm{hole},\alpha+\beta|\beta}(r_2|r_1)$ can both be written exactly as the square of an orbital (see section 3).

When we work with the spin-integrated total spatial densities $\Gamma^{(2)}(r_1|r_2)$ and $\rho(r_1)$, we can only define a total conditional density and a total hole density. The total hole density can actually be written as a weighted sum of $\rho^{\mathrm{hole},\alpha+\beta|\alpha}(r_2|r_1)$ and $\rho^{\mathrm{hole},\alpha+\beta|\beta}(r_2|r_1)$

$$
\begin{aligned}
\rho^{\mathrm{cond}}(r_2|r_1) &= \frac{\Gamma^{(2)}(r_1,r_2)}{\rho(r_1)} \\
&= \frac{\Gamma^{(2)\alpha\alpha}(r_1,r_2)+\Gamma^{(2)\alpha\beta}(r_1,r_2)}{\rho(r_1)} \\
&\quad + \frac{\Gamma^{(2)\beta\alpha}(r_1,r_2)+\Gamma^{(2)\beta\beta}(r_1,r_2)}{\rho(r_1)} \\
&= \frac{\rho^{\alpha}(r_1)}{\rho(r_1)}\rho^{\mathrm{cond},\alpha+\beta|\alpha}(r_2|r_1) \\
&\quad + \frac{\rho^{\beta}(r_1)}{\rho(r_1)}\rho^{\mathrm{cond},\alpha+\beta|\beta}(r_2|r_1) \\
&= \rho(r_2) + \left(\frac{\rho^{\alpha}(r_1)}{\rho(r_1)}\rho^{\mathrm{hole},\alpha+\beta|\alpha}(r_2|r_1)\right. \\
&\quad \left. + \frac{\rho^{\beta}(r_1)}{\rho(r_1)}\rho^{\mathrm{hole},\alpha+\beta|\beta}(r_2|r_1)\right) \\
&= \rho(r_2) + \rho^{\mathrm{hole}}(r_2|r_1). \qquad (\mathrm{A}\,9)
\end{aligned}
$$

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