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FEATURE ARTICLE

# A Quantum Chemical View of Density Functional Theory

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A comparison is made between traditional quantum chemical approaches to the electron correlation problem and the one taken in density functional theory (DFT). Well-known concepts of DFT, such as the exchange−correlation energy $E_{xc} = \int \rho(\mathbf{r})\, \epsilon_{xc}(\mathbf{r})\, d\mathbf{r}$ and the exchange−correlation potential $v_{xc}(\mathbf{r})$ are related to electron correlation as described in terms of density matrices and the conditional amplitude (Fermi and Coulomb holes). The Kohn−Sham one-electron or orbital model of DFT is contrasted with Hartree−Fock, and the definitions of exchange and correlation in DFT are compared with the traditional ones. The exchange−correlation energy density $\epsilon_{xc}(\mathbf{r})$ is decomposed into kinetic and electron−electron potential energy components, and a practical way of calculating these from accurate wave functions is discussed, which offers a route to systematic improvement. $v_{xc}(\mathbf{r})$ is likewise decomposed, and special features (bond midpoint peak, various types of step behavior) are identified and related to electronic correlation.

## 1. Introduction

There has been in recent years a sharp increase in the number of molecular electronic structure calculations based on density functional theory (DFT). Over the years, extensive validation of proposed functionals[1−13] has been carried out for elementary second- and third-row molecules (among these the G1 and G2 sets)[10,12−27] and for transition-metal complexes and organometallic systems,[28−31] for transition states in reactions,[32−38] and, more recently, for charge-transfer complexes.[39] The gradient-corrected exchange functional of Becke,[7] and the correlation functionals of Lee, Yang, and Parr,[8] based on the Colle−Salvetti[40] correlation energy expression, and of Perdew and collaborators[6,10] prove to be particularly accurate, with often even improved accuracy coming from the hybrid functionals introduced by Becke.[25,26] At the same time the local nature of the effective potential in the one-electron Kohn−Sham equations affords efficient computational schemes. The evaluation of matrix elements of the Kohn−Sham exchange−correlation potential always requires at some step a 3D numerical integration. The Diophantine method introduced by Ellis[41] has been the first 3D numerical integration method applied succesfully to molecular electronic structure calculations, but the problem of carrying out 3D numerical integration for poyatomic systems to arbitrary precision was only solved in the mid eighties by Boerrigter *et al.*[42,43] and Becke.[44] The remaining Coulomb problem (the two-electron integrals “bottleneck”) has been addressed by the introduction of auxiliary basis sets (“density fitting”) by Baerends *et al.*[45] These authors applied the expansion of the density in an auxiliary basis set in combination with the use of Slater-type orbitals (STOs) and numerical integration of the Fock matrix elements (see for a different, though related, development: Ellis and co-workers[46−49] and Delley[50]). In these approaches nonstandard basis sets are used (STOs, numerical atomic orbitals), but Sambe and Felton[51] noted that the density-fitting method could equally well be applied with Gaussian basis sets. This allows one to stick more closely to standard quantum chemistry codes, with analytical integral evaluations for all operators except the exchange−correlation potential. Dunlap *et al.*[52] have formulated a variationally stable form of the density fitting. There is currently a revival of

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interest in these techniques,[53,54] and also their applicability in an *ab initio* context is being investigated.[55,56]

Although the high degree of reliability of the DFT calculations based on the present functionals, usually referred to as generalized gradient approximations (GGA), and their computational expedience are well established, still several elements of density functional theory that are particularly relevant for molecular applications remain relatively unknown among quantum chemists. There also remain questions regarding the status of important ingredients of the theory such as the Kohn–Sham orbitals: are they mere mathematical constructs to build the exact (correlated) density from a one-electron model or do they have some physical sense, similar to the Hartree–Fock orbitals or to orbitals of more approximate one-electron theories such as extended Hückel or to natural orbitals? What is the precise meaning of the central quantity of DFT, the exchange–correlation functional $E_{xc}$? Is it equal to the traditional correlation energy of quantum chemistry (exact minus Hartree–Fock energy) plus the Hartree–Fock exchange energy, or plus the exchange energy evaluated with Kohn–Sham orbitals, or again something different? How precisely is correlation incorporated in a one-electron theory like Kohn–Sham?

We will address these questions from a quantum chemical point of view in the sense that we will use the traditional ways in which quantum chemists describe electron correlation: in terms of one- and two-electron density matrices and the more pictorial Fermi and Coulomb holes based on them. We will show that the Kohn–Sham form of density functional theory can be very simply related to the concepts that quantum chemists have build up over the years to describe the electronic structure of atoms and molecules. We will also demonstrate that there are ways to systematically improve upon the present day model functionals in case they would fail (which fortunately does not often seem to be the case). It is possible to construct rigorously correct exchange–correlation energy densities and Kohn–Sham potentials, to which one might take recourse in order to construct improved models might the current ones fail.

This article is structured in the following way. After an introduction into DFT (section 2) the physics of electronic correlation is discussed in section 3 in terms of density matrices and Fermi and Coulomb holes, and the difference between the way the Hartree–Fock model on the one hand and the Kohn–Sham model on the other hand treats (or fails to treat) the correlation is demonstrated. The difference between the definition of the correlation energy in the two models is highlighted. In section 4 the decomposition of both the exchange–correlation energy density $\epsilon_{xc}(\mathbf{r})$ and the exchange–correlation potential $v_{xc}(\mathbf{r})$ into meaningful components is derived. A method is proposed to obtain an exact (very accurate) representation of these spatial functions from an exact (very accurate) wave function. Examples of accurate correlation energy densities and Kohn–Sham potentials are given for a few simple systems (He, $H_2$ at $R_e$ and at large bond distance) in section 5. Section 6 finally presents an analysis of the response part of the Kohn–Sham potential, $v^{resp}$.

## 2. Hohenberg–Kohn and Kohn–Sham Formulations of Density Functional Theory

We present a few aspects of DFT, without any attempt at completeness or rigor (see textbooks[57–59]). Just those features are highlighted that we need in the subsequent development.

For a many-particle system with some two-particle interaction, where all particles move in a given local potential $v(\mathbf{r})$, and with a restriction to systems that have nondegenerate ground states, the first Hohenberg–Kohn theorem (HK-I[60]) states that there is a one-to-one mapping between the potential $v(\mathbf{r})$, the particle density $\rho(\mathbf{r})$, and the ground state wave function $\Psi_0$,

$$\text{(HK-I)} \qquad \rho(\mathbf{r}) \leftrightarrow v(\mathbf{r}) \leftrightarrow \Psi_0 \tag{2.1}$$

This is actually a rather direct consequence of the variational principle. It implies that given a potential, the wave function and density that correspond to it are uniquely determined. Conversely, and this was less intuitively obvious, given a density, only one potential and wave function correspond to that density, so $\Psi_0$ is a functional of $v$ and a functional of $\rho$,

$$\Psi_0 = \Psi_0[v] = \Psi_0[\rho] \tag{2.2}$$

We will be concerned with systems of electrons moving in the field of fixed nuclei, so the external potential $v$ is always just the nuclear field, the two-particle interaction is $1/r_{12}$, and the Hamiltonian is

$$\hat{H} = \hat{T} + \hat{V} + \hat{W} \tag{2.3}$$

$$\hat{T} = \sum_{i=1}^{N} -\frac{1}{2}\nabla^2(i); \quad \hat{V} = \sum_{i=1}^{N} v(\mathbf{r}_i) = \sum_{i=1}^{N}\sum_{\alpha=1}^{A} \frac{-Z_\alpha}{|\mathbf{R}_\alpha - \mathbf{r}_i|};$$

$$\hat{W} = \sum_{i<j}^{N} 1/r_{ij}$$

The HK theorem implies that all properties are functionals of the ground state density, since any property may be determined as the expectation value of the corresponding operator, $\hat{O}$ say, and the wave function is determined by $\rho$,

$$O[\rho] = \langle \Psi_0[\rho] | \hat{O} | \Psi_0[\rho] \rangle \tag{2.4}$$

In particular the kinetic energy is also a functional of the density, $T[\rho]$, as is the electron–electron interaction energy $W[\rho]$. These functionals are called universal since they do not contain the external potential $v$ explicitly, and in principle would only have to be determined once and for all. However, a functional like $T[\rho]$ does depend on the use of a specific form of the two-particle interaction $\hat{W}$. If for instance we would be dealing with noninteracting particles ($\hat{W} = 0$), the ground state wave function belonging to a given $\rho$ would be a single determinant, $\Psi_s[\rho]$, different from the wave function $\Psi[\rho]$ of the fully interacting system, and the external potential $v_s$ corresponding to $\rho$ in the case of noninteracting particles would be different from the $v$ corresponding to $\rho$ in the case of interacting particles. The kinetic energy functional for noninteracting particles

$$T_s[\rho] = \langle \Psi_s[\rho] | \hat{T} | \Psi_s[\rho] \rangle \tag{2.5}$$

will be different from $T[\rho]$.

Clearly the total energy is also a functional of the ground state density. There is, however, a subtle point here: the operator $\hat{O}$ in (2.4) now being the Hamiltonian, we should be clear about the potential $v(\mathbf{r})$ to be used in the Hamiltonian. There are two main possibilities. If for each $\rho$ we take the potential $v(\mathbf{r})$ that corresponds to it according to HK-I, we obtain the functional $E[\rho]$ that yields at each $\rho$ the ground state energy of the unique system having this $\rho$ as its ground state density. We note in passing that not much is known about analytic properties (extrema, continuity) of $E[\rho]$. If, on the other hand, we take a fixed potential $v(\mathbf{r})$, for which $\Psi_0$ is the ground state and $E_0$ the corresponding ground state energy, and evaluate for each $\rho$ the expectation value of the Hamiltonian with this fixed $v$ for $\Psi[\rho]$, we obtain a functional $E_v[\rho]$ which, according to the variation theorem, will have $E_0$ as lower bound

$$\text{(HK-II)} \qquad E_v[\rho] = \langle \Psi[\rho]|\hat{T} + \hat{V} + \hat{W}|\Psi[\rho]\rangle \geq E_0 \tag{2.6}$$

This theorem was formulated by Hohenberg and Kohn[60] and is usually referred to as the second Hohenberg−Kohn theorem (HK-II). For a system of noninteracting electrons and a given external potential $v_s$ the variationally stable energy functional would simplify to

$$E_s[\rho] = \langle \Psi_s[\rho]|\hat{T} + \hat{V}_s|\Psi_s[\rho]\rangle = T_s[\rho] + \int v_s(\mathbf{r})\rho(\mathbf{r})\,\mathrm{d}\mathbf{r} \geq E_{s,0} \tag{2.7}$$

At this point one may wonder how much has been achieved since there is no prescription to find $\Psi_0[\rho]$ from a given density, except the somewhat uninteresting one where one would determine the number of electrons by integration of $\rho$ over space, and the positions and charges of the nuclei from the cusps of $\rho$ so that, the Hamiltonian being determined now, one is back at the traditional problem of solving the Schrödinger equation. However, we will see below that even as a mere existence theorem the HK-I theorem can be quite useful, and it justifies of course the search for functionals of the density for such important quantities as the kinetic and electron−electron interaction energies.

We may contrast the density functional expression for the kinetic and electron−electron interaction energies with the traditional expressions using density matrices.[61−65] It is well known that knowledge of the complete wave function is not required to obtain these quantities. For the kinetic energy it is sufficient to know the one-electron density matrix defined as

$$\gamma(1;1') = N\int \Psi(1,2,...,N)\Psi^*(1',2,...,N)\,\mathrm{d}2\,...\,\mathrm{d}N \tag{2.8}$$

where the diagonal element $\gamma(1;1) \equiv \rho(1)$ is the probability to find an electron with coordinates 1 (position $\mathbf{r}_1$, spin $s_1$). The kinetic energy is

$$T = \langle\hat{T}\rangle = \int_{1\to1'} -\frac{1}{2}\nabla^2(1)\gamma(1,1')\,\mathrm{d}1 \tag{2.9}$$

and requires the *full* one-matrix, including the off-diagonal elements. The electron−electron interaction energy may be written in terms of the diagonal elements, $\Gamma(1,2) = \Gamma(1,2;1,2)$ of the two-electron density matrix, or two-density for short,

$$\Gamma(1,2;1',2') = N(N-1)\int \Psi(1,2,3,...,N)\Psi^*(1',2',3,...,N)\,\mathrm{d}3\,...\,\mathrm{d}N \tag{2.10}$$

The diagonal $\Gamma(1,2)$ represents the probability to find two electrons simultaneously at "positions" 1 and 2, and the ratio $\Gamma(1,2)/\rho(1)$ represents the conditional probability to find an electron at 2 when there is known to be one at 1,

$$\rho^{\text{cond}}(2|1) \equiv \Gamma(1,2)/\rho(1) \tag{2.11}$$

and

$$W = \langle\hat{W}\rangle = \frac{1}{2}\int \frac{1}{r_{12}}\Gamma(1,2)\,\mathrm{d}1\,\mathrm{d}2 = \frac{1}{2}\int \mathrm{d}1\,\rho(1)\int \frac{\rho^{\text{cond}}(2|1)}{r_{12}}\,\mathrm{d}2 \tag{2.12}$$

These expressions demonstrate the well-known fact that in principle the total wave function, with its complicated dependence on $N$ electron coordinates, is not necessary to obtain the energy; the reduced one- and two-matrices are sufficient.[61,62] However, it has for a long time been considered essential that to obtain the electron−electron interaction energy one would need explicit knowledge concerning the conditional probability to find the remaining electrons around a given one. The HK theorem broke away from this accepted belief.

Virtually all applications of DFT in quantum chemistry use the Kohn−Sham one-electron formulation of DFT.[66] We may introduce it by postulating the existence of an "auxiliary" system of $N$ *noninteracting* electrons moving in an external local potential, called $v_s(\mathbf{r})$, which has the property that its wave function—a single Slater determinant of the lowest $N$ orbitals—will yield precisely the same electron density as the exact interacting electron system with potential $v(\mathbf{r})$. So the Kohn−Sham Hamiltonian is just a sum of one-electron Hamiltonians,

$$\hat{H}_s = \sum_i \hat{h}_s(i) = \sum_i\left(-\frac{1}{2}\nabla^2(i) + v_s(\mathbf{r}_i)\right)$$

$$\hat{h}_s(1)\phi_i(1) = \epsilon_i\phi_i(1)$$

$$\Psi_s = |\phi_1(1)\phi_2(2)\,...\,\phi_N(N)|$$

$$\rho_s(\mathbf{r}) = \sum_{i=1}^{N}\sum_s |\phi_i(\mathbf{r},s)|^2 = \rho^{\text{exact}}(\mathbf{r}) \tag{2.13}$$

One may wonder if there could be many potentials $v_s(\mathbf{r})$ with the property that their first $N$ occupied orbital densities sum up to the exact density. The HK-I theorem, however, proves that $v_s(\mathbf{r})$ must be unique. The theorem does not rely on the form of the two-electron interaction, so also if $\hat{W} = 0$, the theorem implies that density and potential are one-to-one related. This proves that $v_s(\mathbf{r})$, if it exists, is unique. Does it always exist? We refer to the literature for discussions of this so-called problem of the noninteracting $v_s$-representability of a density $\rho(\mathbf{r})$.[67−70] Taking the existence of $v_s(\mathbf{r})$ for granted for the molecules the quantum chemists are usually interested in, we note that the Kohn−Sham one-electron model takes a position in DFT that is reminiscent of the one that Hartree−Fock takes in *ab initio* quantum chemistry. In fact, in some respects it is more fundamental since it is not (at least not only) the first, necessarily not exact, step in a sequence of increasingly accurate wave functions, but it is a one-electron model that is intimately related to the *exact* solution of the many-electron problem. Let us cite a few properties of $v_s(\mathbf{r})$ which are relevant in this respect.

(1) $v_s(\mathbf{r})$ is a unique local potential connected with the interacting many-electron system. This point has just been discussed.

(2) $v_s(\mathbf{r})$ yields the *exact* one-electron density $\rho(\mathbf{r})$. This is an important difference with Hartree−Fock, which leads to interesting consequences for the composition of the correlation energy, as will extensively be discussed below.

(3) $\epsilon_{\text{HOMO}} = -\text{IP}^{\text{exact}}$. The property that the highest occupied Kohn−Sham orbital energy is equal to the exact first ionization energy of the system[71,72] is directly related to the fact that the asymptotic behavior of the density is governed by the first ionization energy.[73] If the density is composed of a finite number of Kohn−Sham orbitals, this asymptotic behavior of the density is in turn determined by the one-electron energy of the highest occupied orbital, which necessarily has to be equal to the IP. This is a property that is very desirable in molecular orbital (MO)-based perturbation treatments (PMO theory) or in qualitative MO theory in general and is often simply assumed in such theories. Unfortunately, the Kohn−Sham potentials derived from the local-density approximation (LDA) or the current GGA functionals have very poor asymptotic behavior and lead to an artificial upshift of the one-electron energies by

typically some 5 eV. This can be remedied by constructing potentials with better asymptotic behavior,[74] which is in fact important when considering properties that depend on the the tail of the density, such as dipole[75,76] and higher[77] polarizabilities. [We note in passing that the upshift of the one-electron energies in an LDA or GGA calculation, which persists down to the core levels, implies that $\sum n_i\epsilon_i$ has a considerable error. On the other hand, the total energy in the GGA approximation does not nearly exhibit such a large error (see the comparison between GGA errors in $\epsilon$ and in $E_{\text{total}}$ in ref 78). If one writes the total energy as $\sum n_i\epsilon_i$ minus correction terms for double-counting of electron−electron interaction, $E = \sum n_i\epsilon_i - \int\rho(1)\rho(2)/r_{12}\ \mathrm{d}1\ \mathrm{d}2 + (E_{\text{xc}} - \int\rho v_{\text{xc}}\ \mathrm{d}\tau)$, this implies that there is a compensating error in the other terms. In view of the deficiencies in the GGA approximation to the response part of the exchange−correlation potential,[78] the compensating error most probably involves the term $-\int\rho v^{\text{resp}}\ \mathrm{d}\tau$, which is part of $(E_{\text{xc}} - \int\rho v_{\text{xc}}\ \mathrm{d}\tau)$. See below for definition and discussion of these quantities.]

(4) $\epsilon_{\text{LUMO}}$ (and all other virtual orbital energies) are solutions in exactly the same potential as the occupied orbitals. They are therefore not upshifted in the same way as Hartree−Fock virtual orbitals are. Hartree−Fock orbital energy differences are not estimates of excitation energies, they have to be combined with appropriate $J$ and $K$ integrals.[62] The Kohn−Sham orbital energy differences, however, play a role as a first approximation to the excitation energy in the treatment of excitation energies using time-dependent DFT.[79−82] It has actually been observed empirically for a long time that these orbital energy differences are good approximations to excitation energies, and some very interesting observations concerning the relationship between virtual-occupied Kohn−Sham orbital energy differences and excitation energies have recently been made.[83] At this point we leave it at noting that the virtual Kohn−Sham orbital energies may serve well in qualitative MO considerations. Their precise relationship with excitation energies will hopefully be clarified further by developments in excitation energy calculations using time-dependent DFT.

(5) $v_s(\mathbf{r})$ and components of $v_s(\mathbf{r})$ have remarkable structure, such as peaks at intershell regions in atoms,[84−86,74,78] a peak at the bond midpoint in a molecule,[87−90] step behavior in atoms in going from one shell to the next,[91,78,92] and step behavior in a heteronuclear molecule when going from one atom to the next.[93] These features are directly related to specific aspects of electron correlation. Since the Kohn−Sham orbitals and $v_s(\mathbf{r})$ are connected with the exact correlated system, one may loosely say that all effects of electron correlation “have been folded” into the simple one-electron potential $v_s(\mathbf{r})$. It is the purpose of this contribution to clarify how exactly this is to be understood.

We conclude this section by noting that the abovementioned properties highly recommend the Kohn−Sham orbitals and one-electron energies as tools in the traditional qualitative MO considerations on which much of the rationalizations of contemporary chemistry are based.[94−98] It would be hard to find a better MO theoretical context to apply concepts such as “charge control” and “orbital control” than the Kohn−Sham one-electron model. In case there is some fear that the Kohn−Sham orbitals mysteriously and uncontrolably deviate from the expected behavior, in terms of bonding and antibonding character and behavior under perturbations (geometrical distortions, interaction with other atoms/molecules), we will show below that such fear is unwarranted since the effective one-electron potential $v_s$ is physically very appropiate. One may take the view that the Kohn−Sham orbitals are just another set of one-particle states, as so many have been proposed (Hartree−Fock orbitals, natural orbitals, Brueckner orbitals, Dyson amplitudes), which may very well be used to construct a one-determinantal wave function, $\Psi_s$. Of course this cannot be the exact wave function, and the Kohn−Sham orbitals generally serve a different purpose than creating a reasonable single-determinantal wave function, but there is no reason to shy away from this Kohn−Sham determinantal wave function any more than, *e.g.*, from the Hartree−Fock wave function.

## 3. The Physics of Correlation and the Hartree−Fock and Kohn−Sham One-Electron Theories

The exact total energy may be written as

$$E = \langle\hat{T}\rangle + \langle\hat{V}\rangle + \langle\hat{W}\rangle$$

$$= \int_{1\to1'} -\frac{1}{2}\nabla^2(1)\gamma(1,1')\ \mathrm{d}1 + \int\rho(\mathbf{r})v(\mathbf{r})\ \mathrm{d}\mathbf{r} + \frac{1}{2}\int\frac{1}{r_{12}}\Gamma(1,2)\ \mathrm{d}1\ \mathrm{d}2 \quad (3.1)$$

We may break down the correlated probability $\Gamma(1,2)$ of finding two electrons at 1 and 2 into the independent particle part, which is just the product of the one-electron probabilities $\rho(1)\rho(2)$ and a remainder which can be called the exchange−correlation part of $\Gamma$, $\Gamma_{\text{xc}}$,

$$\Gamma(1,2) = \rho(1)\rho(2) + \Gamma_{\text{xc}}(1,2) \quad (3.2)$$

When an electron is known to be at position 1, the conditional probability $\rho^{\text{cond}}(2|1) = \Gamma(1,2)/\rho(1)$ of the other electrons to be at position 2 around the reference electron at position 1 can be written as the sum of the unconditional probability (the electron density) $\rho(2)$ and the exchange−correlation hole

$$\rho^{\text{cond}}(2|1) = \rho(2) + \frac{\Gamma_{\text{xc}}(1,2)}{\rho(1)} = \rho(2) + \rho_{\text{xc}}^{\text{hole}}(2|1) \quad (3.3)$$

$$\int\rho^{\text{cond}}(2|1)\ \mathrm{d}2 = N - 1$$

The hole $\rho_{\text{xc}}^{\text{hole}}(2|1)$ describes how this conditional density deviates from the unconditional density $\rho(2)$. Since the conditional density integrates to $N - 1$ electrons, the hole integrates to $-1$. More specifically, the integral over all space of the hole in the probability density of electrons with the same spin as the reference electron ($s_2 = s_1$) will be $-1$, and the integral over all space of the hole in the probability density of electrons with the opposite spin ($s_2 \neq s_1$) will be 0: $\int\rho_{\text{xc}}^{\text{hole}}(\mathbf{r}_2,s_2{=}s_1|1)\ \mathrm{d}\mathbf{r}_2 = -1$; $\int\rho_{\text{xc}}^{\text{hole}}(\mathbf{r}_2,s_2{\neq}s_1|1)\ \mathrm{d}\mathbf{r}_2 = 0$. Due to the Pauli principle, which forbids two electrons to be at the same spatial position when they have the same spin, the hole in the density of electrons with the same spin as the reference electron has, for $\mathbf{r}_2 \to \mathbf{r}_1$, to become equal to minus the density of electrons with this spin: $\rho_{\text{xc}}^{\text{hole}}(\mathbf{r}_2{\to}\mathbf{r}_1,s_2{=}s_1|1) = -\rho(1)$. The precise shape of the hole depends strongly on the system, but in general in high-density regions in atoms and molecules the hole in the density of electrons with the same spin as the reference electron will have largest depth around position 1 and will go to zero far from 1, where the presence of the reference electron at 1 is no longer felt. The hole in the density of opposite spin electrons will be much smaller. However, in low-density regions—or in a low-density electron gas—the hole in the density of opposite spin electrons may be of comparable depth and extent, although of course it has to integrate to 0 rather than $-1$.

The two-electron part of the total energy may be broken up accordingly

$$W = \frac{1}{2}\int \frac{\Gamma(1,2)}{r_{12}}\,\mathrm{d}1\,\mathrm{d}2 = \frac{1}{2}\int \frac{\rho(1)\rho(2)}{r_{12}}\,\mathrm{d}1\,\mathrm{d}2 + \frac{1}{2}\int \frac{\Gamma_{\mathrm{xc}}(1,2)}{r_{12}}\,\mathrm{d}1\,\mathrm{d}2$$

$$= \frac{1}{2}\int \rho(1)V_{\mathrm{Coul}}(1)\,\mathrm{d}1 + \frac{1}{2}\int \rho(1)v_{\mathrm{xc}}^{\mathrm{hole}}(1)\,\mathrm{d}1 = W_{\mathrm{Coul}} + W_{\mathrm{xc}} \tag{3.4}$$

which defines the Coulomb potential $V_{\mathrm{Coul}}$ and the exchange−correlation hole potential $v_{\mathrm{xc}}^{\mathrm{hole}}$ at the position 1 of the reference electron as the potentials of the full electronic density $\rho(2)$ and the exchange−correlation hole density $\rho_{\mathrm{xc}}^{\mathrm{hole}}(2|1)$, respectively ($V_{\mathrm{Coul}}$ is sometimes called the *Hartree potential* $V_{\mathrm{H}}$, and another name for the hole potential $v_{\mathrm{xc}}^{\mathrm{hole}}$ is *screening potential* $v_{\mathrm{scr}}$ *cf.*[91]). We note in passing that it is customary in the physics literature to use the pair correlation factor $g(1,2)$, in terms of which the conditional density, hole density and exchange−correlation part of $W_{\mathrm{xc}}$ can also be defined

$$\rho^{\mathrm{cond}}(2|1) = g(1,2)\,\rho(2) = \rho(2) + \frac{\Gamma_{\mathrm{xc}}(1,2)}{\rho(1)}$$

$$\rho_{\mathrm{xc}}^{\mathrm{hole}}(2|1) = \frac{\Gamma_{\mathrm{xc}}(1,2)}{\rho(1)} = (g(1,2) - 1)\rho(2)$$

$$W_{\mathrm{xc}} = \frac{1}{2}\int \frac{\rho(1)(g(1,2) - 1)\rho(2)}{r_{12}}\,\mathrm{d}1\,\mathrm{d}2 \tag{3.5}$$

The pair correlation factor (in the present definition, which uses spatial plus spin coordinates) will be 1, so the hole has zero depth, when 2 is at large distance from 1. It will go to 0, *i.e.* the hole gets full depth $-\rho(1)$, when $2 \to 1$ (including $s_2 = s_1$) on account of the Pauli principle. The hole induced in the electron distribution of other spin electrons around an electron at $1 = \mathbf{r}_1 s_1$, described by $g(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2)$ with $s_1 \neq s_2$, need not have full depth $-\rho(\mathbf{r}_1 s_2)$, corresponding to $g(\mathbf{r}_1 s_1; \mathbf{r}_1 s_2 {\neq} s_1) = 0$, since different spin electrons retain some probability to be at the same position. In fact, in low-density regions $g(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2 {\neq} s_1)$ does tend to to 0 for $\mathbf{r}_2 \to \mathbf{r}_1$, but in high-density regions this is known not to be the case.

Let us now consider the definition of exchange and correlation in density functional theory. We wish to strongly emphasize that these quantities do not have the same meaning in DFT as in *ab initio* quantum chemistry.

Starting with the exchange energy, let us consider the energy of the Kohn−Sham determinantal wave function, *i.e.* the expectation value of $\Psi_s$ with respect to the full Hamiltonian,

$$E^{\mathrm{KS}} = \langle \Psi_s | \hat{H} | \Psi_s \rangle = T_s + \int \rho v\,\mathrm{d}\mathbf{r} + \frac{1}{2}\int \rho V_{\mathrm{Coul}}\,\mathrm{d}\mathbf{r} + W_{\mathrm{x}} \tag{3.6}$$

This defines the exchange energy $W_{\mathrm{x}}$ of DFT as a Hartree−Fock type exchange energy, but evaluated with the Kohn−Sham orbitals. [We continue denoting all purely electron−electron interaction energy terms with $W$, subscripted as the case requires; other names for the exchange energy of DFT, each with its own merits, are $E_{\mathrm{x}}$, or $U_{\mathrm{x}}$, or $E_{\mathrm{xc},\lambda=0}$ or $V_{\mathrm{ee}}^{\lambda=0} - U$.] The kinetic energy $T_s$ is simply the kinetic energy of the Kohn−Sham orbitals. Since the exact density $\rho(\mathbf{r}) = \sum_{s1}\rho(1)$ determines $v_s(\mathbf{r})$ and therefore the Kohn−Sham (KS) orbitals, $T_s$ and $W_{\mathrm{x}}$ are functionals of the density. So the exchange energy may be written,

$$W_{\mathrm{x}} = -\frac{1}{2}\int \frac{|\gamma_s(1,2)|^2}{r_{12}}\,\mathrm{d}1\,\mathrm{d}2$$

$$\gamma_s(1,2) = \sum_i^N n_i \phi_i(1)\phi_i^*(2) \tag{3.7a}$$

The conditional density of the KS determinant will by definition only have the exchange or Fermi hole, which may be given in terms of the exchange part $\Gamma_{\mathrm{x}} = -\gamma_s(1,2)\,\gamma_s(2,1)$ by which the two-electron density matrix $\Gamma_s$ of the KS determinantal wave function differs from the independent particle term $\rho(1)\rho(2)$:

$$\Gamma_s(1,2) = \rho(1)\rho(2) - \gamma_s(1,2)\gamma_s(2,1)$$

$$\Gamma_{\mathrm{x}}(1,2) = -\gamma_s(1,2)\gamma_s(2,1) = -\,|\gamma_s(1,2)|^2$$

$$\rho_{\mathrm{x}}^{\mathrm{hole}}(2|1) = \frac{-|\gamma_s(1,2)|^2}{\rho(1)}$$

$$W_{\mathrm{x}} = \frac{1}{2}\int \rho(1)\rho_{\mathrm{x}}^{\mathrm{hole}}(2|1)\frac{1}{r_{12}}\,\mathrm{d}2\,\mathrm{d}1 = \frac{1}{2}\int \rho(1)v_{\mathrm{x}}^{\mathrm{hole}}(1)\,\mathrm{d}1 \tag{3.7b}$$

We work with pure spin orbitals $\phi_{\mathrm{i}}(1) = \varphi_i(\mathbf{r}_1)\sigma_i(s_1)$, where $\varphi_i$ is the spatial part of $\phi_i$ and $\sigma_i$, the spin part, is either $\alpha$ or $\beta$. So if $\phi_i(1)$ is an up-spin orbital, $\phi_i(1) = \varphi_i(\mathbf{r}_1)\alpha(s_1)$, it will be zero if 1 has down spin ($s_1 = -{}^1/_2$), and *vice versa*. Taking this into account in the above expressions for $\gamma_s(1,2)$, $\rho_{\mathrm{x}}^{\mathrm{hole}}$ leads immediately to the well-known properties of the Fermi hole of a one-determinantal wave function[99] that it is definite negative, consists of the same-spin density as the reference electron, and has for $2 \to 1$ (implying equal spins) a depth equal to the density of electrons with the same spin as the reference electron

$$\rho_{\mathrm{x}}^{\mathrm{hole}}(2{\to}1|1) = -\rho(1) \tag{3.8}$$

and *zero* depth for opposite spin electrons

$$\rho_{\mathrm{x}}^{\mathrm{hole}}(\mathbf{r}_2, s_2{\neq}s_1|1) = 0 \tag{3.9}$$

The present definition of the exchange energy and the Fermi hole differs only from the traditional one in that the KS orbitals are used rather than the Hartree−Fock orbitals. Still, this leads to a considerable advantage when it comes to defining the correlation or Coulomb hole. It is natural to define as the Coulomb hole the difference between the exact conditional density and the conditional density that has been used to define the Fermi hole.[100] Since $\rho^{\mathrm{cond,KS}}(2|1) = \rho(2) + \rho_{\mathrm{x}}^{\mathrm{hole}}(2|1)$, this is, with the present definitions, equal to the difference between the full exchange−correlation hole and the Fermi hole

$$\rho_{\mathrm{c}}^{\mathrm{hole}}(2|1) = \rho^{\mathrm{cond}}(2|1) - \rho^{\mathrm{cond,KS}}(2|1) = \rho_{\mathrm{xc}}^{\mathrm{hole}}(2|1) - \rho_{\mathrm{x}}^{\mathrm{hole}}(2|1) \tag{3.10}$$

If we would take Hartree−Fock as our reference one-determinantal state, the difference between the conditional densities will not just be the difference between the full hole and the (Hartree−Fock) exchange hole but will include a term describing the difference between the exact and Hartree−Fock densities,

$$\rho_c^{\text{hole,HF}}(2|1) = \rho^{\text{cond}}(2|1) - \rho^{\text{cond,HF}}(2|1) = (\rho(2) - \rho^{\text{HF}}(2)) + \rho_{\text{xc}}^{\text{hole}}(2|1) - \rho_{\text{x}}^{\text{hole,HF}}(2|1) \quad (3.11)$$

The term $\Delta\rho(2) = \rho(2) - \rho^{\text{HF}}(2)$ may not be small (see below), in particular when compared to the difference between the full and exchange holes, and in a way would contaminate the definition of the Coulomb correlation hole. Using the definition (3.10) we write the correlation part $W_c$ of the two-electron energy as

$$W_c = W_{\text{xc}} - W_{\text{x}} = \frac{1}{2}\int \rho(1)\rho_c^{\text{hole}}(2|1)\frac{1}{r_{12}}\,\text{d}2\,\text{d}1 = \frac{1}{2}\int \rho(1)v_c^{\text{hole}}(1)\,\text{d}1 \quad (3.12)$$

From the definition it is obvious that the Coulomb hole integrates to zero. Many examples of Fermi and Coulomb holes are provided in refs 100 and 101, from which certain characteristics can be deduced. In atoms, the Coulomb hole has a typical "polarization" shape: if the reference position is close to the nucleus, probability ("charge density") is lowered around the nucleus and enhanced at the outside of the atom; if the reference position is at the outside, the reverse "polarization" takes place; if the reference position is in between, in the middle of the electron cloud, charge is "pushed away" around the reference electron and increases at the backside of the nucleus. The Coulomb hole for an electron pair bond will be discussed below.

Turning now to the definition of the correlation energy, we note that for a long time quantum chemists have agreed to define the correlation energy as the difference between the exact and Hartree–Fock energies, $E_{\text{corr}} = E - E^{\text{HF}}$. The well-known quantity $E_{\text{xc}}$ of DFT is however *not* the sum of $W_x^{\text{HF}}$ and $E_{\text{corr}}$ (and neither of $W_x$ and $E_{\text{corr}}$). We arrive at $E_{\text{xc}}$ by following Kohn and Sham[66] in writing the exact total energy not in the traditional way

$$E = T + \int \rho v\,\text{d}\mathbf{r} + \frac{1}{2}\int \rho V_{\text{Coul}}\,\text{d}\mathbf{r} + W_{\text{xc}} \quad (3.13)$$

but, using $T_s$, as

$$E = T_s + \int \rho v\,\text{d}\mathbf{r} + \frac{1}{2}\int \rho V_{\text{Coul}}\,\text{d}\mathbf{r} + E_{\text{xc}} \quad (3.14)$$

Since all other quantities in this expression are defined, this equation defines $E_{\text{xc}}$

$$E_{\text{xc}} = (T - T_s) + W_{\text{xc}} = T_c + W_{\text{xc}} \quad (3.15)$$

where we have introduced the usual notation $T_c$ for the correlation correction (with respect to $T_s$) to the kinetic energy. It is customary to define as the correlation energy $E_c$ of DFT the nonexchange part of $E_{\text{xc}}$, $E_c = E_{\text{xc}} - W_x$. (n.b. to distinguish traditional quantities, such as the Hartree–Fock exchange energy, from the present DFT quantities, we will give them the explicit superscript HF. $E_c^{\text{HF}}$ will be used to denote the traditional correlation energy.) Evidently, the correlation energy of DFT is just the difference between the exact energy (3.14) and the Kohn–Sham determinantal energy (3.6),

$$E_c = E_{\text{xc}} - W_x = E - E^{\text{KS}} \quad (3.16)$$

Since the Hartree–Fock determinant is by definition the one with the lowest possible energy, $E^{\text{KS}}$ must necessarily be higher than $E^{\text{HF}}$, and the DFT correlation energy must be more negative (larger in an absolute sense) than the traditional correlation energy.[102,103]

$$E_c \le E_c^{\text{HF}} \quad (3.17)$$

**TABLE 1: Contributions (in eV) to the Traditional Correlation Energy $E_c^{\text{HF}}$ for Selected Molecules**

| | $E_c^{\text{HF}}$ | $T_c^{\text{HF}}$ | $V_c^{\text{HF}}$ | $W_{\text{Coul,c}}^{\text{HF}} + W_c^{\text{HF}}$ |
|---|---|---|---|---|
| $H_2$ ($R = R_e$) | −1.1 | +1.3 | −0.5 | −1.9 |
| $H_2$ ($R = 5.0$ au) | −3.9 | +8.9 | −8.5 | −4.4 |
| $H_2$ ($R = 10.0$ au) | −6.3 | +7.9 | −8.4 | −5.6 |
| $MnO_4^-$ | −14.4 | +35.7 | −115.5 | +65.4 |
| $Ni(CO)_4$ | −3.4 | −35.0 | +147.8 | −116.3 |
| $Cr(CO)_6$ | −4.5 | −4.5 | +30.8 | −30.8 |
| He | −1.1 | +1.1 | −0.1 | −2.1 |
| $H_2O$ | −7.0 | +6.5 | +1.0 | −14.5 |
| Ne | −8.9 | +8.3 | +1.3 | −18.5 |
| $N_2$ | −11.1 | +13.7 | −13.8 | −11.0 |

The correlation energy as defined here consists of only two terms, a kinetic and an electron–electron interaction part,

$$E_c = T_c + W_c \quad (3.18)$$

The difference between the DFT and traditional definitions of correlation is often ignored and correlation functionals are usually judged by their performance in reproducing the traditional correlation energy, which is often the only one known to a reasonable degree of accuracy. It has indeed been demonstrated that the traditional and DFT definitions do not differ much for two-electron atoms.[103] However, we wish to stress that the difference is rather essential,[104] if not numerically then at least conceptually. Since the Hartree–Fock energy uses the Hartree–Fock one-electron density $\rho^{\text{HF}}$

$$E^{\text{HF}} = T^{\text{HF}} + \int \rho^{\text{HF}} v\,\text{d}\mathbf{r} + \frac{1}{2}\int \frac{\rho^{\text{HF}}(1)\rho^{\text{HF}}(2)}{r_{12}}\,\text{d}1\,\text{d}2 + W_x^{\text{HF}} \quad (3.19)$$

which differs from the exact density by an amount $\Delta\rho = \rho - \rho^{\text{HF}}$, the traditional correlation energy may be written as

$$\begin{aligned} E_c^{\text{HF}} &= E - E^{\text{HF}} \\ &= T - T^{\text{HF}} + \int \Delta\rho v\,\text{d}\mathbf{r} + \int \frac{\Delta\rho(1)\rho(2)}{r_{12}}\,\text{d}1\,\text{d}2 + \frac{1}{2}\int \frac{\Delta\rho(1)\Delta\rho(2)}{r_{12}}\,\text{d}1\,\text{d}2 + W_{\text{xc}} - W_x^{\text{HF}} \quad (3.20) \\ &= T_c^{\text{HF}} + V_c^{\text{HF}} + W_{\text{Coul,c}}^{\text{HF}} + W_c^{\text{HF}} \end{aligned}$$

The terms $T_c^{\text{HF}}$ and $W_c^{\text{HF}}$ of $E_c^{\text{HF}}$ will be different from the corresponding terms $T_c$ and $W_c$ of $E_c$, sometimes quite essentially so, as we will see below, but $E_c^{\text{HF}}$ also contains the additional terms $V_c^{\text{HF}}$, the correlation correction to the electron–nuclear potential energy, and $W_{\text{Coul,c}}^{\text{HF}}$, the correlation correction to the Coulombic part of the electron–electron potential energy. These two terms of course also make $E_{\text{xc}}^{\text{HF}} = W_x^{\text{HF}} + E_c^{\text{HF}}$ essentially different from $E_{\text{xc}}$,

$$\begin{aligned} E_{\text{xc}} &= T_c + W_{\text{xc}} \\ E_{\text{xc}}^{\text{HF}} &= T_c^{\text{HF}} + W_{\text{xc}} + V_c^{\text{HF}} + W_{\text{Coul,c}}^{\text{HF}} \quad (3.21) \end{aligned}$$

In order to appreciate the difference between $E_c^{\text{HF}}$ and $E_c$, we have given in Table 1 the various terms of $E_c^{\text{HF}}$, for a series of common molecules.[100,101] The CI calculations from which these numbers have been derived have yielded a large percentage of the correlation energy for the light systems, but not nearly so for the transition metal complexes.[100,105,106] The numbers will only be used qualitatively here. We first observe that the widespread feeling that the electron density is described well by the Hartree−Fock wave function and that correlation mainly affects the two-electron part of the energy by building a proper Coulomb hole around a reference electron, is not corroborated by the results in the table. A striking example is dissociating $H_2$ (the comparison is with a *restricted* Hartree−Fock wave function). Taking the correlation correction to the electron−nuclear energy $V_c^{HF}$ as a measure of the quality of the Hartree−Fock electron density, it is clear that this density must be very poor at larger bond distances. Not even at the equilibrium distance is $V_c^{HF}$ really small, but it becomes even much larger than the electron−electron correlation energy at 5.0 and 10.0 bohr. Both the one-electron terms $V_c^{HF}$ and $T_c^{HF}$ are much larger than the electron−electron term, and at 10.0 bohr the electron−nuclear correlation energy is the largest of all terms. It should be appreciated that a Kohn−Sham calculation (again we just take a *restricted* calculation) would for $H_2$ at large distance give the exact density, and therefore the $V_c$ term would disappear, but also that the kinetic correlation energy $T_c$ would be 0[107] since the Kohn−Sham orbital would in the region around each hydrogen atom be just a hydrogenic 1s atomic orbital, yielding the right limiting kinetic energy of two hydrogen atoms. Before we continue to analyze the $H_2$ case in more detail, it should be clear that this example, even if somewhat special, is by no means exceptional in having large correlation terms associated with density changes. The transition metal complexes, even if the CI calculations were far from complete, show tremendous correlation energies, in particular in view of the usually rather weak coordination bond. Note that in $MnO_4^-$ the electron−electron energy *increases*, indicating closer proximity of the electrons as a consequence of electron correlation. The correlation effects in this molecule have been discussed extensively in ref 105. As a matter of fact, only the very light systems such as He conform to the expectation that the $V_c^{HF}$ term will be small and that the correlation correction to the potential energy is mostly an electron−electron interaction energy correction. In this case, in keeping with the virial relationship, the total correlation correction to the electron−electron interaction energy, $W_{Coul,c}^{HF} + W_c^{HF}$, is about twice as large as the correlation energy which itself is equal (but with opposite sign) to the kinetic correction $T_c^{HF}$. A simple molecule like $N_2$ however, has a very large electron−nuclear correlation energy, considerably larger than the electron−electron term. This demonstrates that the DFT correlation energy, with a zero electron−nuclear term, even if it would not numerically differ much from the traditional correlation energy, will have a very different composition.

In order to understand these results better, and to prepare for the discussion of the Kohn−Sham potential and the exchange−correlation energy density in the next section, we show in Figure 1 plots of the Fermi, Coulomb, and total holes in $H_2$ at various distances.[100,101] The Fermi hole in a two-electron system only consists of the self-interaction correction and is equal to the density of the electron with the same spin as the reference electron, which is half the total density. Although the hole is only plotted for a reference electron at a position 0.3 bohr at the left of the right nucleus, it should be emphasized that the Fermi hole is completely independent of the position of the reference electron. It is totally inadequate as an approximation to the total hole, in particular at long bond distances. At such distances, a reference electron close to the right nucleus should experience the nuclear attraction of that nucleus unscreened, and it will not be perturbed much by the fully screened nucleus of the other H atom. The Fermi hole, however, removes only half of the density, not the complete density, around the electron's own nucleus, so that the nucleus is (incorrectly) partly screened and the electron will respond by building a too diffuse orbital. This is putting in the language of "effective one-electron potentials" the well-known deficiency of the Hartree−Fock wave function, leading to unwarranted ionic configurations. It should be realized, however, that the largest effect is not an error in the two-electron part of the energy but that the one-electron density becomes so diffuse that the largest error occurs in the electron−nuclear energy.

The Coulomb hole has the typical shape of creating a hole around the reference electron and causing buildup of charge further away at the other nucleus (the Coulomb hole integrates to zero). At a large interatomic distance the Coulomb hole obviously takes care that the total hole around the reference electron is equal to the total density at that nucleus, and at the other nucleus it cancels the Fermi hole, so the full electron density is undisturbed at the other hydrogen atom, as it should. It is important to note that the Coulomb and total holes cannot be static. When the reference position moves along the bond axis and crosses the bond midpoint, the hole will have to switch to the other nucleus. So the total hole will be invariant with respect to the reference position when it is somewhere in the neighborhood of one nucleus, but there will be a region of rapid change in the neighborhood of the bond midpoint.

The too weak nature of the Fermi hole around the reference electron and its static nature are deficiencies that make the Hartree−Fock model seriously deficient in any electron pair bond, more so in weaker bonds and when there are multiple bonds. Extreme examples occur for bonds involving transition metal atoms, *e.g.* the 5-fold bond between Mn and the $O_4$ cage in $MnO_4^-$ [105] (*cf.* also $MnO^+$ [108]) and the famous case of $Cr_2$ with a weak 6-fold bond, *cf.* discussion in ref 109.

As we have argued here, the DFT definition of the correlation energy has some aesthetically and physically appealing features. Nevertheless, it has the major drawback that it is not a good operational definition, as the traditional one is. It is not at all easy to obtain the Kohn−Sham limit of an atom or molecule. If an exact or very accurate wave function is not known, this is at present impossible; even if the latter is known it is by no means straightforward to obtain the KS determinantal wave function, though progress is being made.[74,89,90,110−112]

## 4. The Exact (DFT) Exchange−Correlation Energy Density and the Kohn−Sham Potential

We first show that the Kohn−Sham one-electron operator $\hat{h}_s$ differs from the Fock operator $\hat{f}$ only in that the exchange part of $\hat{f}$ is replaced by the local potential $v_{xc}(\mathbf{r}) = \delta E_{xc}[\rho]/\delta\rho(\mathbf{r})$. Note that $E_{xc}$ is a functional of $\rho$ since all the other terms in 3.14 are functionals of $\rho$. Replacing in the variationally stable functional $E_v[\rho]$ [(2.6)] $T[\rho] + W_{xc}[\rho]$ by $T_s[\rho] + E_{xc}[\rho]$ (which defines $E_{xc}[\rho]$) we obtain

$$E_v[\rho] = T_s[\rho] + \int v(1)\rho(1)\,\mathrm{d}1 + \frac{1}{2}\int \rho(1)V_{Coul}(1)\,\mathrm{d}1 + E_{xc}[\rho] \quad (4.1)$$

We use for simplicity of notation space-spin coordinates (like $1 = \mathbf{r}_1 s_1$) throughout, although the external potential is as usual assumed to be spin-independent $((v(\mathbf{r}_1, +{}^1/_2) = v(\mathbf{r}_1, -{}^1/_2) = v(\mathbf{r}_1))$ and also the Coulomb potential is only $\mathbf{r}$-dependent. $E_v[\rho]$ attains its minimum value at the ground state density $\rho_0$, so

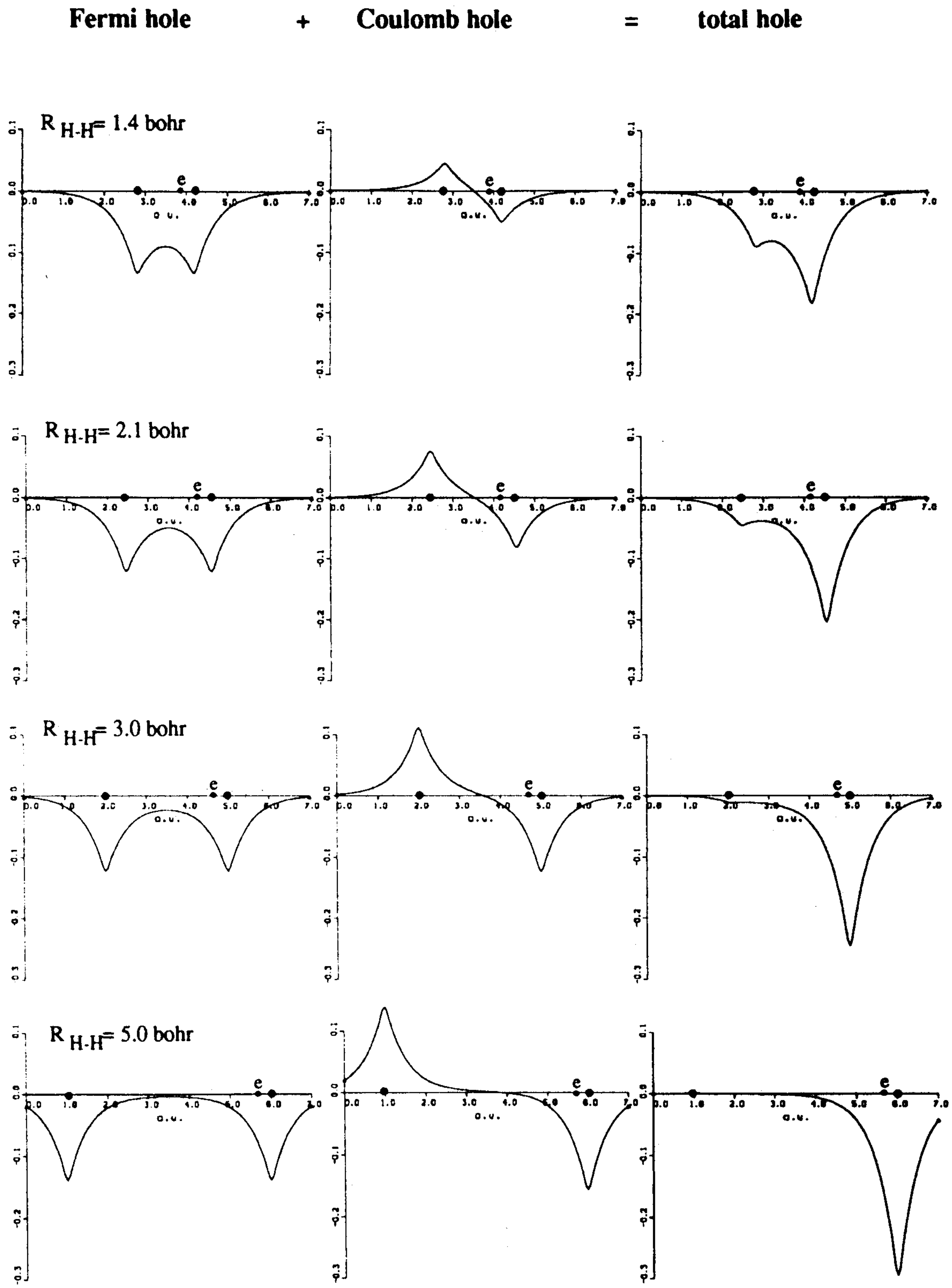

**Figure 1.** The Fermi hole, Coulomb hole, and total hole in the $H_2$ molecule at various values of the internuclear distance. In all plots the reference electron is placed 0.3 bohr to the left of the right nucleus. Nuclear positions are indicated with black dots on the axis.

using the Lagrange multiplier $\mu$ to keep the density properly normalized to $N$ electrons, the variational stability requires that

$$\frac{\delta}{\delta\rho}[E_v[\rho] - \mu(\textstyle\int \rho(1)\,\mathrm{d}1 - N)]_{\rho_0} = 0$$

$$\frac{\delta T_s}{\delta\rho(1)}|_{\rho_0} + v(1) + V_{\mathrm{Coul}}(1) + \frac{\delta E_{\mathrm{xc}}}{\delta\rho(1)}|_{\rho_0} - \mu = 0 \quad (4.2)$$

Also the functional $E_s[\rho]$ [(2.7) for the noninteracting system] attains its minimum for the density $\rho_0$, since $v_s$ is by definition the potential for which the ground state density of the noninteracting system is identical to the one for the interacting system,

$$\frac{\delta}{\delta\rho}[E_s[\rho] - \mu(\textstyle\int \rho(1)\,\mathrm{d}1 - N)]_{\rho_0} = 0$$

$$\frac{\delta T_s}{\delta\rho(1)}|_{\rho_0} + v_s(1) - \mu = 0 \quad (4.3)$$

This shows that $v_s$ is, apart from a constant, equal to the functional derivative of $T_s$, and the question of the existence of

$\upsilon_s$ is equivalent to the question of existence of this functional derivative. The possibility that we have a spin-polarized system with different Kohn−Sham potentials for different spins, *i.e.* $\upsilon_s(\mathbf{r}_1,s_1 = {}^1/_2) = \upsilon_{s,\alpha}(\mathbf{r}_1)$ different from $\upsilon_s(\mathbf{r}_1,s_1 = -{}^1/_2) = \upsilon_{s,\beta}(\mathbf{r}_1)$, is automatically accounted for through our use of space-spin coordinates, although we will not explicitly use it in this paper. In that case the functional derivative with respect to the density of up-spin electrons, $\delta T_s/\delta\rho(\mathbf{r}_1,s_1 = {}^1/_2) = \delta T_s/\delta\rho_\alpha(\mathbf{r}_1)$, yielding $\upsilon_{s,\alpha}(\mathbf{r}_1)$, may differ from that with respect to down-spin electrons. Eliminating $\delta T_s/\delta\rho$ from (4.2) and (4.3) and writing $\upsilon_{xc} = \delta E_{xc}[\rho]/\delta\rho$, we obtain for $\upsilon_s$, apart from a constant,

$$\upsilon_s(1) = \upsilon(1) + V_{\mathrm{Coul}}(1) + \upsilon_{xc}(1) \tag{4.4}$$

$E_{xc}$ and $\upsilon_{xc}$ are obviously the crucial quantities of DFT. Traditional *ab initio* quantum chemistry tries to improve properties, in particular energetics, basically by trying to increase the accuracy of the wave function. Density functional methods on the other hand try to obtain good energetics by trying to develop more accurate models for the exchange−correlation energy density per particle $\epsilon_{xc}$, from which the exchange−correlation energy $E_{xc}$ may be obtained

$$E_{xc} = \int \rho(1)\epsilon_{xc}(1)\,\mathrm{d}1 \tag{4.5}$$

$\epsilon_{xc}$ should be a functional of the density, and models have been derived initially from the electron gas, using at point **r** the properties of the homogeneous electron gas with uniform density $\rho$ equal to the density $\rho(\mathbf{r})$ that the finite system has locally (the local-density approximation). The gradient expansion for systems of varying electron density has some difficulties, so generalized gradient approximations have been developed for the exchange part[5,7,10] and correlation part[6,8,10] that express $\epsilon_{xc}$ in terms of local properties of the density at point **r** (its value, and the value of the gradient or Laplacian),

$$\epsilon_{xc}^{\mathrm{GGA}}(1) \approx f(\rho(1),\nabla\rho(1),\nabla^2\rho(1),...) \tag{4.6}$$

We may also exploit the essential simplicity of $E_{xc}$ (it just consists of the two terms $W_{xc}$ and $T_c$) to obtain and study the exact $\epsilon_{xc}$.[90,113] Introducing the so-called kinetic potentials $\upsilon_{\mathrm{kin}}$ and $\upsilon_{s,\mathrm{kin}}$[87,91,93] we may write

$$E_{xc} = W_{xc} + T - T_s = \frac{1}{2}\int \rho(1)\,\upsilon_{xc}^{\mathrm{hole}}(1)\,\mathrm{d}1 + \int \rho(1)(\upsilon_{\mathrm{kin}}(1) - \upsilon_{s,\mathrm{kin}}(1))\,\mathrm{d}1 \tag{4.7}$$

The hole potential $\upsilon_{xc}^{\mathrm{hole}}$ has already been introduced, but in order to clarify the physical meaning of the kinetic potentials we need to factorize the wave function $\Psi$ in the so-called marginal ($(\rho/N)^{1/2}$) and conditional ($\Phi$) probability amplitudes introduced by Hunter[114]

$$\Psi(1,2,...,N) = \sqrt{\frac{\rho(1)}{N}}\,\Phi(2,...,N|1) \tag{4.8}$$

The conditional probability amplitude $\Phi$ describes all effects of electron correlation, since its square

$$|\Phi(2,...,N|1)|^2 = \frac{|\Psi(1,2,...,N)|^2}{\rho(1)/N} \tag{4.9}$$

represents the probability distribution of the other electrons around a reference electron at position 1. The kinetic potential is related to the rate of change of the conditional probability distribution of the other electrons with respect to change in the position of the reference electron[87]

$$\upsilon_{\mathrm{kin}}(1) = \frac{1}{2}\int |\nabla_1\Phi(2,...,N|1)|^2\,\mathrm{d}2\,...\,\mathrm{d}N = \frac{\nabla_{1'}\nabla_1\gamma(1,1')|_{1\to 1'}}{2\rho(1)} - \frac{|\nabla_1\rho(1)|^2}{8\rho(1)^2} \tag{4.10}$$

There are two well-known situations where the exchange−correlation hole rapidly changes with reference position. The first is related to change of the Fermi hole. The Fermi hole is known to have approximately the shape of the localized orbital at reference positions where most of the total charge can be ascribed to one particular localized orbital.[115] When the reference position crosses the border region between the localized orbitals, the Fermi hole undergoes rapid change. In atoms the Fermi hole is to a large degree localized within the shell where the reference position is located (the atomic shells are not only energetically but also spatially quite well separated) and rapid "jumping" of the hole occurs when going from one atomic shell to the next. This leads to peaks in $\upsilon_{\mathrm{kin}}$ in atoms[87] which we will not discuss here. In the case of an electron pair bond we have noted the rapid change of the Coulomb hole when the reference position crosses the bond midpoint. It has indeed been observed that $\upsilon_{\mathrm{kin}}$ exhibits a sharp peak around the bond midpoint in $H_2$ at large bond distance.[87]

It has been shown that the kinetic energy can be written as the sum of the so-called Weizsäcker kinetic energy, which is $N$ times the kinetic energy of an electron in the "density orbital" $(\rho/N)^{1/2}$ and the integral of the density times the kinetic potential

$$T_{\mathrm{W}} = N\int \sqrt{\frac{\rho}{N}}\left(-\frac{1}{2}\nabla^2\right)\sqrt{\frac{\rho}{N}}\,\mathrm{d}\mathbf{r}$$

$$T = T_{\mathrm{W}} + \int \rho\upsilon_{\mathrm{kin}}\,\mathrm{d}1$$

$$T_s = T_{\mathrm{W}} + \int \rho\upsilon_{s,\mathrm{kin}}\,\mathrm{d}1 \tag{4.11}$$

Since the density is exactly the same for the Kohn−Sham wave function and the exact wave function, $T_{\mathrm{W}}$, is the same for $T$ and $T_s$, so indeed

$$T_c = \int \rho(\upsilon_{\mathrm{kin}} - \upsilon_{s,\mathrm{kin}})\,\mathrm{d}1 = \int \rho\upsilon_{c,\mathrm{kin}}\,\mathrm{d}1 \tag{4.12}$$

The kinetic correlation energy density per particle $\upsilon_{c,\mathrm{kin}} = \upsilon_{\mathrm{kin}} - \upsilon_{s,\mathrm{kin}}$, which is written as a potential for reasons to become clear below, is truly related to the Coulomb correlation. The Kohn−Sham determinant $\Psi_s$ and the related conditional probability amplitude $\Phi_s$ embody only the Fermi hole, so $\upsilon_{s,\mathrm{kin}}$, which is related to $\Phi_s$ by (4.10), only reflects the mobility of the Fermi hole. In the electron pair bond we have seen that $\upsilon_{\mathrm{kin}}$ will exhibit a peak at the bond midpoint due to the switching of the Coulomb hole from one nucleus to the other. $\upsilon_{s,\mathrm{kin}}$, however, is everywhere zero in a two-electron system since the Fermi hole is completely static. This follows also immediately when one writes $\upsilon_{s,\mathrm{kin}}$ in terms of molecular orbitals, which is possible in view of the simple one-determinantal nature of $\Psi_s$

$$\upsilon_{s,\mathrm{kin}}(1) = \frac{1}{2}\int |\nabla_1\Phi_s(2...N|N)|^2\,\mathrm{d}2\,...\,\mathrm{d}N = \frac{1}{2}\sum_{i=1}^{N}|\nabla_1\frac{\phi_i(1)}{\sqrt{\rho(1)}}|^2 \tag{4.13}$$

Since in the closed shell two-electron case there is only one doubly occupied Kohn−Sham orbital with $\phi_1(1) = (\rho(1))^{1/2}$ $\upsilon_{s,\mathrm{kin}}$ will be zero.

We now obtain the following simple and closely related expressions for the exchange−correlation energy density and the exchange−correlation potential

$$\epsilon_{xc} = \frac{1}{2}v_{xc}^{hole} + v_{c,kin}$$

$$v_{xc} = v_{xc}^{hole} + v_{c,kin} + v^{resp} \tag{4.14}$$

These are the central equations of this paper. The functional differentiation of $E_{xc}[\rho] = \int \rho\epsilon_{xc}([\rho];1)\,d1$ leads immediately to the terms $v_{xc}^{hole}$ and $v_{c,kin}$ in $v_{xc}$ (the factor of $^1/_2$ in front of in the expression for $\epsilon_{xc}$ disappears in $v_{xc}$ due to the double occurrence of $\rho$ in (3.5) for $W_{xc}$). The response term $v^{resp}$ of $v_{xc}$ contains the terms with functional derivatives of the kinetic potentials and the pair correlation function $g(1,2)$[91] (see (6.1)). We will defer a discussion of the so-called response part of $v_{xc}$, $v^{resp}$,[78,91−93] which will be the least familiar entity in (4.14), to section 6.

Since we have shown how these quantities are related to the exact wave function, we may actally obtain them from exact (very accurate) wave functions and study them. This provides a method to judge existing model expressions for $\epsilon_{xc}$ and $v_{xc}$ and to develop better models when needed. It should be noted, however, that $\epsilon_{xc}$ is not a unique function of **r**. Different spatial functions $\epsilon_{xc}$ may yield the same integrated $E_{xc}$. This is well known for the kinetic energy density, where partial integration may lead to an alternative kinetic energy density that also integrates to the same kinetic energy

$$T = -\int \frac{1}{2}\sum_i n_i\phi_i^*\nabla^2\phi_i\,d1 = +\int \frac{1}{2}\sum_i n_i|\nabla\phi_i|^2\,d1 \tag{4.15}$$

Similarly, an alternative exchange−correlation energy density is often defined by the use of the so-called coupling constant integration,[116−118] which leads to an exchange−correlation energy density $\bar{\epsilon}_{xc}(1)$ that is the potential $\bar{v}_{xc}$ of an "averaged" exchange−correlation hole that has the kinetic effects incorporated. We, however, stick to (4.14) since it follows very straightforwardly from the definition of $E_{xc}$ and has terms that have a clear physical meaning (see also below) and are clearly connected with the corresponding terms in the Kohn−Sham potential (which *is* a unique function of **r**). Moreover, they can be calculated from accurate wave functions, which is at present not possible with the alternative coupling constant integrated $\bar{v}_{xc}$. It is to be emphasized that the potentials $v_{kin}$ and $v_{s,kin}$, and therefore also $v_{c,kin}$, even though they are also (partial) kinetic energy densities, are well-defined functions of **r**. In this context it is interesting to note the equality

$$v_{kin}(1) = \int \Phi^*(2...N|1)\left(-\frac{1}{2}\nabla^2\right)\Phi(2...N|1)\,d2\,...\,dN = \frac{1}{2}\int|\nabla_1\phi(2...N|1)|^2\,d2\,...\,dN \tag{4.16}$$

which is not based on partial integration (the integration is not over coordinate 1) but has been proven in ref 87 from the normalization of $\Phi(2...N|1)$ at any point 1.

Let us consider the calculation of $\epsilon_{xc}$ and $v_{xc}$ of (4.14) from accurate wave functions. The following steps have to be taken: (1) A large-scale CI calculation may provide us with accurate, correlated $\rho(1)$, $\gamma\,(1,1')$, and $\Gamma(1,2)$. (2) $v_{xc}^{hole}(1)$ may be obtained straightforwardly from $\Gamma(1,2)$ and $\rho(1)$,

$$v_{xc}^{hole}(1) = \int \frac{\Gamma(1,2) - \rho(1)\rho(2)}{\rho(1)}\frac{1}{r_{12}}\,d2 \tag{4.17}$$

(3) $v_{kin}$ may be obtained straightforwardly from $\rho(1)$ and $\gamma\,(1,1')$ according to (4.10). (4) $v_{s,kin}$ may be obtained from (4.10) with $\gamma_s(1,1')$ substituted for $\gamma\,(1,1')$, or alternatively from (4.13). Obviously, for this the Kohn−Sham orbitals are needed, which can be obtained if $v_s$ is known. This is actually the hard part of the procedure. Many attempts have been made to generate from a given density $\rho(1)$ the $v_s$ that uniquely corresponds to it.[74,84−87,110,111,119−124] Most of these methods have been applied to atoms, some are indeed only suitable for spherically symmetric and/or few-electron systems. To date, the only methods that have been applied to molecules[89,90,112] are those of Van Leeuwen and Baerends[74,89,90] and the method of Zhao, Morrison, and Parr.[111,112,122] Since the accurate CI density is usually obtained from a Gaussian basis set calculation, there are considerable technical difficulties in obtaining an accurate $v_s$. The "accurate" density is usually inaccurate both close to the nucleus and in the tail of the density due to the properties of the Gaussians. There are also more fundamental problems connected with the requirement of generating the values of the function $v_s(1)$ at all points in space from a set of data that is necessarily limited due to the finiteness of the basis. Fortunately, these problems do not prohibit the generation of reasonable potentials $v_s(1)$ and in particular Kohn−Sham orbitals $\{\phi_i\}$. Only the Kohn−Sham orbitals are needed to obtain $v_{s,kin}$, but $v_s(1)$ is also required if we want to obtain $v^{resp}$, which is just the difference of $v_s$, *i.e.* $v_{xc}$ and the potentials $v_{xc}^{hole}$ and $v_{c,kin}$ that were already determined.

In the next section we will show some exact exchange−correlation energy densities for very simple systems (He, dissociating $H_2$). These at the same time provide, of course, a view of the $v_{xc}^{hole}$ and $v_{c,kin}$ components of the Kohn−Sham potential $v_s$. Some effects of the response part of $v_s$ will be mentioned, but $v^{resp}$ will be discussed more fully in section 6.

## 5. Kohn−Sham Potentials and Correlation Energy Densities in He and H$_2$

In order to focus on the effects of electron correlation, we consider specifically the correlation energy density and the correlation potential

$$W_c = W_{xc} - W_x = \int \rho(1)\epsilon_c(1)\,d1$$

$$\epsilon_c(1) = \frac{1}{2}v_c^{hole}(1) + v_{c,kin}(1) = \frac{1}{2}\int \frac{\Gamma(1,2) - \Gamma_s(1,2)}{\rho(1)}\frac{1}{r_{12}}\,d2 + v_{c,kin}(1)$$

$$v_c(1) = v_{xc}(1) - v_x(1) = v_c^{hole}(1) + v_{c,kin}(1) + v_c^{resp}(1) \tag{5.1}$$

Since $\Gamma_s(1,2)$ is the two-density of the Kohn−Sham one-determinantal wave function $\Psi_s$, it is determined by the one-density $\gamma_s(1,2)$ through the relation $\Gamma_s(1,2) = \rho(1)\rho(2) - \gamma_s(1,2)\gamma_s(2,1)$, *cf.* (3.7b), and can be obtained directly from the Kohn−Sham orbitals. The exchange potential $v_x$ that is subtracted from $v_{xc}$ to obtain the correlation potential, is the potential of the Fermi hole plus a corresponding response part. As a matter of fact, the response part of $v_x$ is zero in two-electron systems, so in the examples below $v_c^{resp}(1)$ is actually also the response part of the full $v_{xc}$ and the c subscript can be omitted. In Figure 2 we show the components $v_{c,kin}$ and $^1/_2v_c^{hole}$ of $\epsilon_c$ for $H_2$ at $R_e$ and at large distance (5.0 au) and for He. Note that at $R_e$ (Figure 2a) the Coulomb hole potential is attractive around the hydrogen nuclei and clearly makes the largest contribution to $\epsilon_c$, but $v_{c,kin}$ is by no means negligible [$v_{c,kin}$ is equal to $v_{kin}$

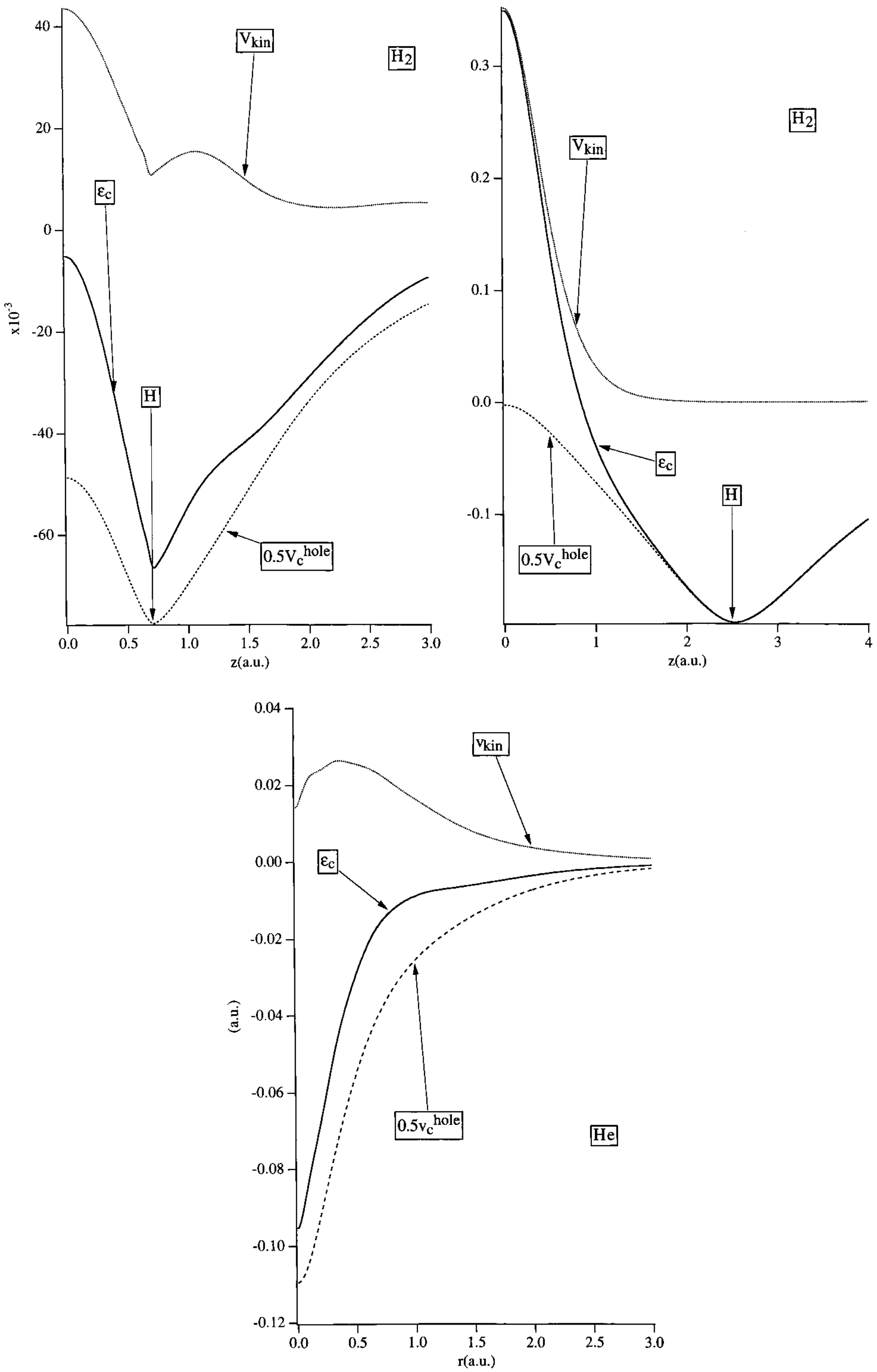

**Figure 2.** The correlation energy density $\epsilon_c(\mathbf{r})$ and its components $v_{c,kin}$ ($= v_{kin}$ in these cases) in three cases: (a) plotted along the bond axis of $H_2$ at $R$(H−H) = 1.401 bohr ($R_e$) (the bond midpoint is at $z$ = 0.0); (b) *idem*, at $R$(H−H) = 5.0 bohr; (c) for He.

in this two-electron case and therefore positive definite according to the defining equation (4.10)]. In particular, $v_{c,kin}$ clearly exhibits a maximum at the bond midpoint, as we expected on the basis of the switching of the Coulomb hole in that region. Considering the corresponding correlation potential $v_c$ in Figure 3a, one notes that the response potential makes a rather strong positive contribution. It diminishes significantly the attractive nature of $v_c^{hole}$ around the nucleus and combined with $v_{c,kin}$ the effect of $v^{resp}$ is to make $v_c$ just positive around the bond midpoint. The relatively small net contracting nature of $v_c$ is in agreement with the relatively small negative electron−nuclear correlation correction of −0.5 eV in Table 1. These effects become magnified in the large-distance situation (R = 5.0 bohr) of Figures 2b and 3b (note the difference in scale with Figures 2a and 3a). The Coulomb hole potential is strongly attractive around the hydrogen nuclei. Since $v^{resp}$ is negligible in this particular case, the Kohn−Sham potential $v_s$ basically differs from the Fock operator (which is also just a local potential in this case) by the terms $v_c^{hole} + v_{c,kin}$, and it is clear that in particular $v_c^{hole}$ will make the Kohn−Sham orbitals much more contracted around the H nuclei than the Hartree−Fock orbitals. This is precisely what is needed of course, since we have seen that the largest error in the Hartree−Fock case was due to the

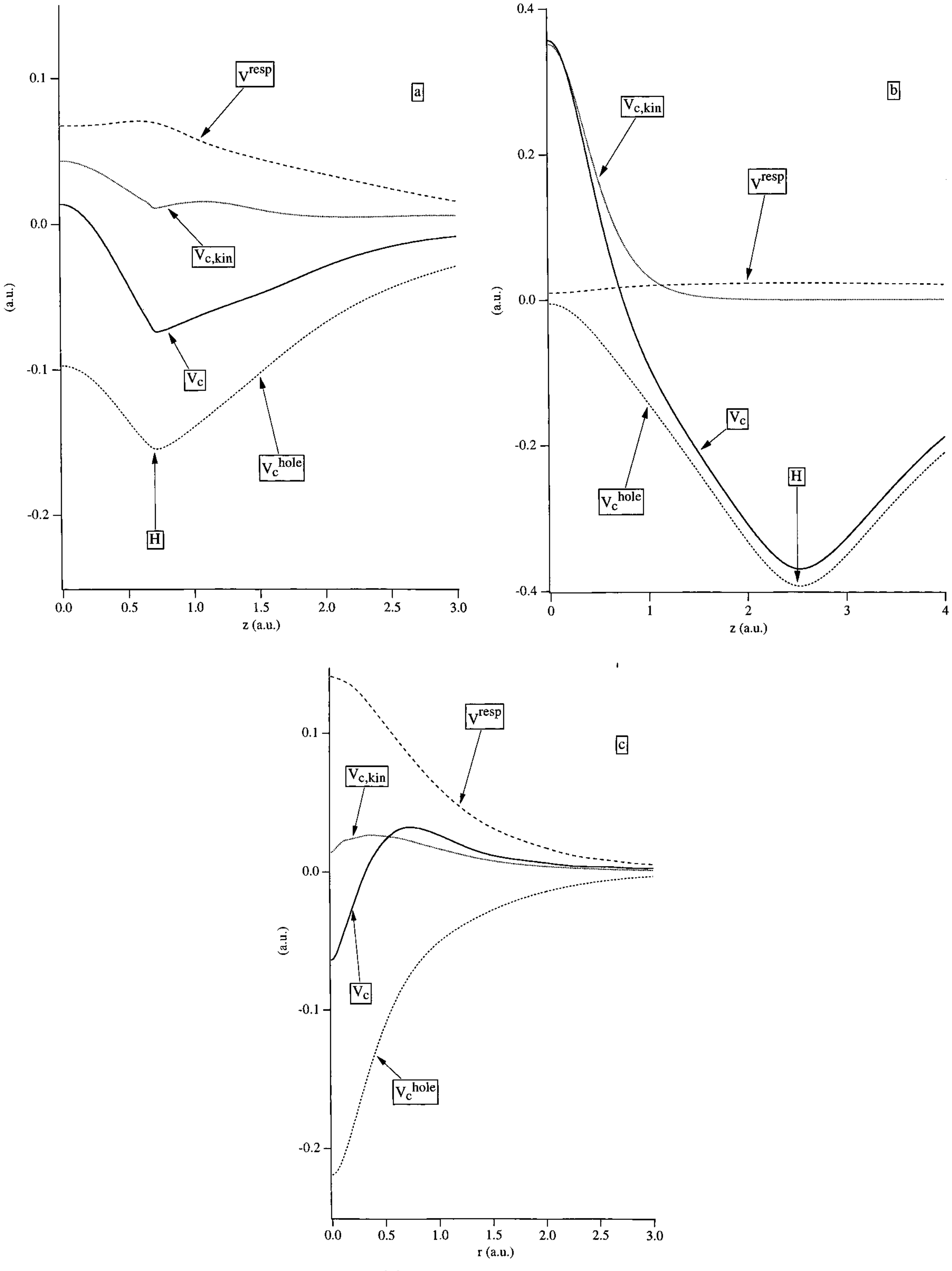

**Figure 3.** The correlation potential $v_c$ and its components $v_c^{\text{hole}}$, $v_{c,\text{kin}}$ ($= v_{\text{kin}}$ in this case), and $v^{\text{resp}}$ ($= v^{N-1}$ in this case) for the cases: (a) plotted along the bond axis of $H_2$ at $R$(H−H) = 1.401 bohr ($R_e$) (the bond midpoint is at $z = 0.0$); (b) *idem*, at $R$(H−H) = 5.0 bohr; (c) for He.

much too diffuse nature of the Hartree−Fock density, caused by the too strong screening of the nuclei by half of the other electron that does not go away to the other nucleus. Equivalently, the exchange hole potential is too weak and has to be deepened by the Coulomb hole potential. The fact that in $v_s$ the full exchange−correlation hole potential $v_{xc}^{\text{hole}}$ features, and not just the Fermi hole potential $v_x^{\text{hole}}$, explains why a restricted Kohn−Sham calculation on dissociating $H_2$ can yield just the sum of two H atom densities. The potential $v_{xc}^{\text{hole}}$ may be considered to incorporate the information on what the conditional probability distribution of the other electrons is "momentarily", *i.e.* when the reference electron is at position 1; the kinetic potential on the other hand is related to the "dynamics" of the hole. It has a large bond midpoint peak in $H_2$ at large bond distance since the Coulomb hole is changing strongly as a function of reference position around the midpoint. The large peak of $v_{c,\text{kin}}$ occurs in a region where the electron density is small. Its contribution to $v_s$ may help to build the exact density, contributing to the "confinement" of charge around the H nucleus by the large wall it provides, but its effect on the energy

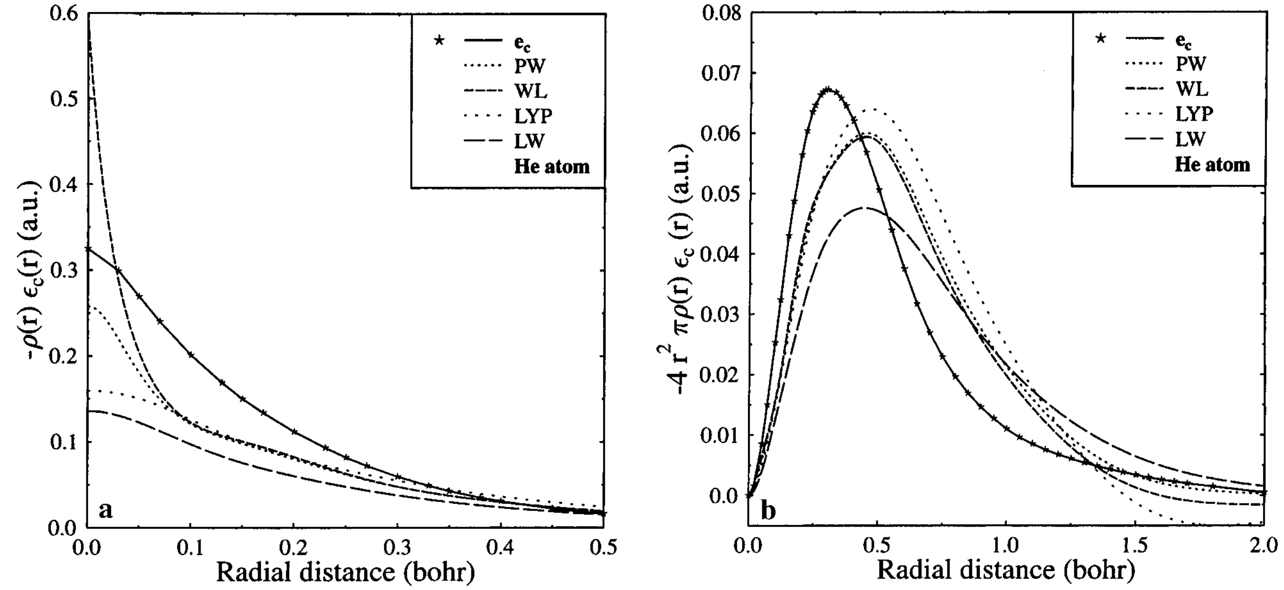

**Figure 4.** Correlation energy density in He compared to a number of model correlation energy densities: PW, Perdew–Wang;[11] WL, Wilson–Levy;[127] LYP, Lee–Yang–Parr;[8] LW, local Wigner.[126] (a) $-\rho(r)\epsilon_c(r)$ from $r = 0.0-0.5$ bohr. (b) $-4\pi\, r^2\rho(r)\epsilon_c(r)$ from $r = 0.0-2.0$ bohr.

by its contribution to $\epsilon_c$ will be very much smaller than the one of $v_c^{hole}$ since the latter is large where the density is also large.

This example also very simply demonstrates how DFT works. Whereas the Kohn–Sham determinantal wave function $\Psi_s$ is, of course, in an energetic sense an even poorer wave function than the Hartree–Fock determinant, the Kohn–Sham potential does build a correct density, much in contrast to Hartree–Fock and mostly by the presence of $v_c^{hole}$ and to some extent $v_{c,kin}$ and $v^{resp}$. The correct energy is then provided by the incorporation in the energy density of the correlation effects, mostly by $^1/_2 v_c^{hole}$ and to some extent by $v_{c,kin}$.

The case of He (Figures 2c and 3c) is interesting since it is the classical case of purely dynamical correlation and it conforms to the expectation of reasonably accurate density at the Hartree–Fock level. The figures show that $v_{c,kin}$ is smaller than $^1/_2 v_c^{hole}$, but it is not completely negligible. If only the components $v_c^{hole}$ and $v_{c,kin}$ of $v_c$ would be present, it is clear that $v_c$ would be rather attractive around the nucleus. It is in this case the response part $v^{resp}$ that actually cancels most of the attraction due to $v_c^{hole}$, so that the total $v_c$ is rather small everywhere and has the characteristic shape, observed by several authors,[84,85,87,119,123] of being attractive close to the nucleus and repulsive further out. $v_c$ does not have a large net effect on the electron density in this case.

It is interesting to make a comparison[113] between the present "exact" correlation energy density (note, however, the remark above about the nonuniqueness of the energy density) and the currently used model correlation energy densities. We take the local-density approximation (LDA) for the correlation energy density in the Perdew–Wang parametrization,[125] the local Wigner (LW) function,[126] and the gradient-dependent Perdew–Wang (PW),[10,11] Lee–Yang–Parr (LYP),[8] and Wilson–Levy (WL)[127] models. In Figure 4 our "exact" $-\rho(r)\epsilon_c(r) = -e_c(r)$ from a large CI calculation on He is compared to the model correlation energy densities. The various model $e_c(r)$ functions have quite different local behavior. In Figure 4a we focus on the inner region, between 0.0 and 0.5 bohr, where the contribution $^1/_2 v_c^{hole}$ dominates (*cf.* Figure 2c). It is known that the Coulomb hole in this region represents mostly in–out correlation, being negative around the nucleus and the reference electron and positive further outward.[100] The resulting negative $^1/_2 v_c^{hole}$ and $\epsilon_c$ in this region are clearly underestimated by all model functionals (except for the nuclear peak of $\epsilon_c^{WL}$ which has no energetic effect due to the vanishingly small volume). Since most of the model energy densities integrate to the correct correlation energy—parameters in all of the model functionals except PW have been fitted to obtain this exactly or approximately for He—the underestimation at small $r$ has to be compensated by overestimation at larger $r$. This is demonstrated in Figure 4b, where the multiplication by $4\pi r^2$ exhibits more clearly the contribution to the integral from various $r$ regions. In the region 0.5–1.4 bohr, where the Coulomb hole has a characteristic polarization shape,[100] all the model energy densities are larger (*i.e.* more negative) than $\epsilon_c$. All the radial functions $-4\pi r^2\rho(r)\epsilon_c^{mod}(r)$ corresponding to model energy densities have their maximum around $r = 0.5$ bohr, while the maximum in $-4\pi r^2\rho(r)\epsilon_c^{mod}(r)$ occurs at somewhat shorter $r$ (ca. 0.3 bohr). In Figure 5 the same comparison is made for the $H_2$ molecule at $R_e$ (Figure 5a) and at large bond distance (5.0 bohr) (Figure 5b). The values of $\rho(z)\epsilon_c(z)$ are plotted for $z$ along the internuclear axis (bond midpoint at $z = 0$). It is clear that there are considerable discrepancies between the "exact" correlation energy density and the model energy densities, as well as large differences among the latter. The models using density gradients were parametrized from atomic data (LYP, WL) or obtained from the gradient expansion for the inhomogeneous electron gas with suitable cutoffs (PW). However, with regard to density gradients there is a basic difference between atoms and molecules. For atoms $|\nabla\rho(\mathbf{r})|$ is never small, while for molecules it is close to zero in the bond midpoint region. One can expect also that correlation effects in this molecular region differ from those in the homogeneous or weakly inhomogeneous electron gas. Because of this, $\epsilon_c^{mod}(\mathbf{r})$ may have a rather accidental behavior in the bond midpoint region. Figure 5a shows that indeed there is rather different behavior of the various energy density functions in the region between the nuclei for the equilibrium H–H distance. The exact $\rho(z)\epsilon_c(z)$ has a pronounced maximum at $z = 0$, approaching zero (from below) at that point. The bond midpoint peak in $v_{c,kin}$ is largely responsible for this; see Figure 2a. The model functionals seem to lack this feature. Although they have maxima at the bond midpoint, they are considerably more shallow functions of $z$ than is $\rho(z)\epsilon_c(z)$. The Wilson–Levy energy density exhibits a sharp minimum at $z = 0$. Around

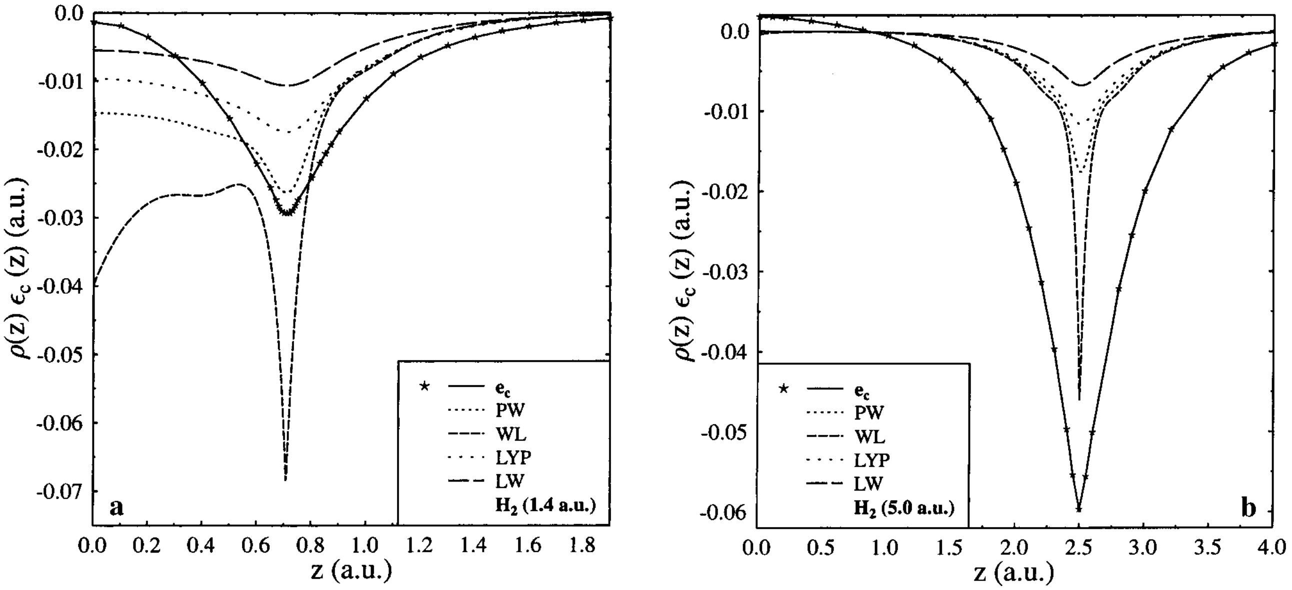

**Figure 5.** Correlation energy density in $H_2$ at $R_e$ (a) and at $R = 5.0$ bohr (b) compared to model correlation energy densities. See caption to Figure 4. $z$ is the coordinate along the internuclear axis; the bond midpoint is at $z = 0.0$.

the nucleus the various model energy density functions are similar to those found for the He atom, as may be expected from their dependence on the density. However, it should be noted that the underlying correlation is very different. The Coulomb hole is now due to left−right correlation rather than in−out correlation. This difference becomes manifest in the outer tail. Whereas in He the model energy densities become more negative than $\rho(z)\epsilon_c(z)$ at distances from the nucleus larger than *ca.* 0.4 bohr, in $H_2$ $\rho(z)\epsilon_c(z)$ remains more negative in the complete tail region. This may be understood from the strong left−right correlation that will be present when the reference electron is at these positions. This difference in the physics of the correlation compared to He is clearly not recognized by the model correlation functionals. Obviously, there will again be compensation of errors, the model functionals giving more negative contributions around the bond midpoint. The failure of the model functionals to describe left−right correlation becomes very clear in the case where this type of correlation becomes very strong, in the near-dissociation situation, $R$(H−H) = 5.0 bohr (Figure 5b). The exact $\rho(z)\epsilon_c(z)$ exhibits wide and deep wells around the nuclei (*cf.* Figure 2b). Contrary to this, all model functionals exhibit much smaller wells around the nuclei. The model energy densities are completely determined by the local electron density and its gradient, which are practically the same as in the H atom. The model functionals cannot recognize from these local properties of the density the strong left−right correlation. They will, in fact, integrate to almost the same correlation energy (−0.03 to −0.06 au) as for the equilibrium H−H distance, whereas the exact correlation energy is −0.3125 au.[128] As a matter of fact, the gradient-corrected density functionals for exchange deviate by approximately the same amount from the exact exchange, so that the total $E_{xc}^{mod}$ is fairly accurate (see ref 107 for a more detailed comparison). The compensation of errors in the correlation functionals by opposite errors in the exchange functionals seems to be fairly systematic, resulting in accurate total $E_{xc}$ values from the existing gradient-corrected total functionals.

We may end this section with a comment on the desirability of separating exchange and correlation. It has been recognized for a long time[2,129,130] that the exchange-only LDA (Xα, $\alpha = {}^2/_3$) hole already captures some essential physics in the case of dissociation or weak interaction by employing, by construction, a hole that is centered around the reference electron (with maximum depth at the reference position). The same holds for the full LDA exchange−correlation hole, not by the use of electron−gas correlation but irrespective of it, simply by the translational symmetry dictated hole-centering around the reference electron, where the hole is dominated by the “exchange” part. References 129 and 130 stress how deficient the Hartree−Fock hole actually is in many cases due to its too diffuse nature. This goes some way in explaining the relative success (if one takes HF as the reference) of a rough hole modeling like that applied in Xα. The results in this section and in section 3 demonstrate how pathetically inadequate the exchange hole is; it makes restricted HF for dissociating unpaired spin systems completely size *in*consistent. One may take the view that the LDA hole is actually overshooting and is too localized around the reference electron and that one should therefore build in some amount of “exact exchange” to make the hole somewhat more diffuse. This is one way to view Becke’s[25,26] successful application of hybrid functionals, which has proven very fruitful for systems at equilibrium geometries. The precise amount of exact exchange may, however, not be the same for all systems and situations. For instance, it is possible to define the amount of pure exchange $W_x$ that has to be mixed with the exchange−correlation part of the two-electron energy $W_{xc}$ to obtain for $E_{xc}$ the exact relation,[107,131]

$$E_{xc} = CW_x + (1 - C)W_{xc} \tag{5.2}$$

and it is then easily demonstrated that in $H_2$ upon dissociation $C$ has to go to zero. This agrees with the unphysical nature of pure exchange at the dissociation limit. It has been suggested to redefine “exchange” so that it incorporates the near-degenaracy correlation we are dealing with in this example.[132] We believe that, for the purpose of hole modeling, our results so far also provide good arguments in favor of dispensing with the distinction between exchange and correlation altogether.

## 6. Response Part of the Kohn−Sham Potential

The response part of the Kohn−Sham potential is probably the least well-known part of $v_s$ and maybe the least physically transparent. It plays, however, a significant role in building the effective one-electron potential of the Kohn−Sham model, as we have seen in the previous section. We therefore discuss its derivation and properties in this section.

Taking the functional derivative of $E_{\mathrm{xc}}$ leads directly to the the potentials $v_{\mathrm{c,kin}} = v_{\mathrm{kin}} - v_{\mathrm{s,kin}}$ and $v_{\mathrm{xc}}^{\mathrm{hole}}$, and, in addition, to terms in which the functional derivatives of these potentials enter:

$$v^{\mathrm{resp}}(1) = \int \rho(1')\frac{\delta v_{\mathrm{kin}}(1')}{\delta\rho(1)}\,\mathrm{d}1' - \int \rho(1')\frac{\delta v_{\mathrm{s,kin}}(1')}{\delta\rho(1)}\,\mathrm{d}1' + \frac{1}{2}\int\frac{\rho(2)\rho(3)}{r_{23}}\,\frac{\delta(g(2,3)-1)}{\delta\rho(1)}\,\mathrm{d}2 + \mathrm{d}3$$

$$= v_{\mathrm{kin}}^{\mathrm{resp}} - v_{s,\mathrm{kin}}^{\mathrm{resp}} + v_{\mathrm{xc}}^{\mathrm{hole,resp}} = v_{\mathrm{c,kin}}^{\mathrm{resp}} + v_{\mathrm{xc}}^{\mathrm{hole,resp}} \qquad (6.1)$$

This potential is a measure of the sensitivity of the correlation, embodied in the conditional probability amplitude and hence in the kinetic potentials and the pair correlation function, to density variations. These density variations are to be understood in the following way. If the density changes to $\rho + \delta\rho$, then according to the Hohenberg−Kohn theorem this changed density corresponds uniquely to an external potential $v + \delta v$ (we only consider densities that are $v$-representable). For the system with external potential $v + \delta v$ we have the corresponding pair-correlation function $g([\rho + \delta\rho];1,2)$ and kinetic potentials. So the derivatives occurring in the response potential may be regarded to reflect the linear response of the system to density changes $\delta\rho$ caused by potential change $\delta v$.

It is gratifying, and a considerable help in understanding the physics of $v^{\mathrm{resp}}$, that it is possible[87] to relate this term in the Kohn−Sham potential, just as the other terms, to the electron correlation as described by the conditional amplitudes $\Phi$ and $\Phi_s$ of the interacting and noninteracting systems respectively. To this end we partition the total Hamiltonians $H^N$ and of the interacting and noninteracting systems respectively.

$$H^N = -\frac{1}{2}\nabla_1^2 + v(1) + \sum_{j=2}^{N}\frac{1}{r_{1j}} + H^{N-1}$$

$$H^{N-1} = \sum_{j=2}^{N}\left\{-\frac{1}{2}\nabla_j^2 + v(j) + \sum_{k>j}^{N}\frac{1}{r_{jk}}\right\} \qquad (6.2)$$

and

$$H_s^N = -\frac{1}{2}\nabla_1^2 + v_s(1) + H_s^{N-1}$$

$$H_s^{N-1} = \sum_{j=2}^{N}\left\{-\frac{1}{2}\nabla_j^2 + v_s(j)\right\} \qquad (6.3)$$

It is possible to write $v^{\mathrm{resp}}$ in terms of expectation values of the $(N-1)$-Hamiltonians with respect to the conditional amplitudes. When the reference electron is at position 1, we may define as the "energy" of the $(N-1)$-electron system described by the conditional amplitude $\Phi$ the expectation value of $H^{N-1}$ with respect to $\Phi$

$$E^{N-1}(1) = \int \Phi^*(2...N|1)H^{N-1}\Phi(2...N|1)\,\mathrm{d}2\,...\,\mathrm{d}N \qquad (6.4)$$

which will, according to the variation theorem, at all positions 1 be higher than the ground state energy of the $(N-1)$-electron system. The definite positive potential $v^{N-1}$ is defined as this difference

$$v^{N-1}(1) = E^{N-1}(1) - E_0^{N-1} \qquad (6.5)$$

It is known that asymptotically, when position 1 goes to infinity, the conditional amplitude tends to the ground state wave function of the $(N-1)$-electron system,[73] so $v^{N-1}$ will tend to zero at inifinity. Similarly we may define for the noninteracting Kohn−Sham system the analogous quantity

$$v_s^{N-1}(1) = \int \Phi_s^*(2...N|1)H_s^{N-1}\Phi_s(2...N|1)\,\mathrm{d}2\,...\,\mathrm{d}N - E_s^{N-1} \qquad (6.6)$$

where it should be noted that $H_s{}^{N-1}$ is the Hamiltonian for $N-1$ noninteracting electrons in the field $v_s$ that belongs to the interacting $N$-electron ground state density. Due to the simple one-electron nature of $H_s{}^{N-1}$ and the one-determinantal form of $\Phi_s$ it is possible to express $v_s{}^{N-1}$ in terms of the Kohn−Sham orbitals and orbital energies

$$v_s^{N-1}(1) = \epsilon_N - \sum_{i=1}^{N}\epsilon_i\,\frac{|\phi_i(1)|^2}{\rho(1)} \qquad (6.7)$$

This proves that in a closed-shell two-electron system, where there is just one Kohn−Sham orbital, $v_s{}^{N-1}$ will be identically zero.

It is now possible to make the identifications[87,91]

$$v^{N-1}(1) = v_{\mathrm{kin}}^{\mathrm{resp}}(1) + v_{\mathrm{xc}}^{\mathrm{hole,resp}} \qquad (6.8)$$

and

$$v_s^{N-1}(1) = v_{s,\mathrm{kin}}^{\mathrm{resp}}(1) \qquad (6.9)$$

so that

$$v^{\mathrm{resp}}(1) = v^{N-1}(1) - v_s^{N-1}(1) \qquad (6.10)$$

Since in He and $H_2$ $v_s{}^{N-1}$ is zero, we can interpret the response potential directly as the energy of the "wave function" $\Phi$ describing the remaining electrons when the reference electron is located at position 1. In the case of $H_2$ at large bond length, it is clear that when the reference electron is at a position close to one nucleus, a say, then $\Phi$ will practically be the 1s wave function of an electron around the H nucleus b. The energy of $\Phi$ will be very close to the ground state energy of the $H_2^+$ system, which will be the energy of H atom b slightly perturbed by proton a at large distance. This explains that $v^{\mathrm{resp}}$ ($= v^{N-1}$) is very small in this case (*cf.* Figure 3b). The fact that the energy of $\Phi$ is a little higher than the ground state energy of $H_2^+$ may be understood as a lack of resonance stabilization from the configuration with the electron at a and the bare proton b. This stabilization will be present in the exact wave function of $H_2^+$ but is lacking in $\Phi$. We can also understand that for He $v^{N-1}$ is no longer negligible (Figure 3c). $\Phi$ describes in this case a one-electron probability density around the He nucleus ($Z = +2$). The Fermi hole is in this case just $-\,{}^1\!/_2\rho(1)$. If $\Phi$ would only describe the Fermi correlation, it would correspond to an electron density equal to half the He ground state density, irrespective of the reference position. This is too diffuse compared to the ground state density of the $\mathrm{He}^+$ ion and the energy of $\Phi$ would be higher than the ground state energy of $\mathrm{He}^+$, yielding a constant positive $v^{N-1}$. Incoporating the Coulomb correlation into $\Phi$ changes the density ${}^1\!/_2\rho(1)$ by the Coulomb hole. According to the Coulomb hole plots of Figure 3.1c of ref 100 this makes the density even more diffuse when the reference position is close to the nucleus, explaining the relatively high positive value of $v^{N-1}$ close to the nucleus. When the reference position moves outward, the Coulomb hole first gets a polarization shape and finally changes to the contraction behavior that reflects the more contracted density of He$^+$ compared to $^1/_2\rho(1)$ of ground state He. $\Phi$ describing then the He$^+$ ion will have an energy equal to the He$^+$ ground state energy, and $v^{N-1}$ will be zero. The situation for H$_2$ at $R_e$ is clearly in between He and H$_2$ at large bond distance.

It is interesting to consider what happens in the case of an electron pair bond between two different nuclei. Suppose the bond is formed between atoms A and B with ionization potentials $I_A$ and $I_B$, respectively, $I_B > I_A$. In order for such a heteronuclear diatomic molecule to dissociate into neutral atoms, the highest doubly occupied Kohn−Sham orbital should at large bond distances be an equal mixture of the A and B atomic orbitals containing the unpaired electrons, since otherwise the atoms would become charged. This problem has been discussed by Perdew[133] and Almbladh and von Barth.[134] These authors have put forward arguments that the Kohn−Sham potential has to exhibit a positive shift

$$\Delta v_s = I_B - I_A \tag{6.11}$$

around the more electronegative atom *B*. This would effectively put the highest atomic orbitals of A and B at the same energy, allowing the required 50-50 mix in the KS highest occupied orbital (HOMO) of the "molecule". It is possible to show that the behavior (6.11) of the KS potential stems from the response part of $v_s$.[93] Let us consider the form of $v^{\rm resp}(1)$ in the region of the HOMO $\phi_N(1)$. Again we may assume, on account of (6.7), that $v_s^{N-1}$ in this region is negligible, since $\phi_N(1)$ constitutes the dominant contribution to $\rho(1)$. Therefore $v^{\rm resp}(1)$ reduces effectively to $v^{N-1}(1)$,

$$v^{\rm resp}(1) \approx v^{N-1}(1) = E^{N-1}(1) - E_0^{N-1} \tag{6.12}$$

Suppose that the reference electron is in the region $\Omega_B$ of the more electronegative atom B, $\mathbf{r}_1 \in \Omega_B$. In this case the conditional amplitude $\Phi(2...N\,|1)$ desribes the $(N-1)$-electron system A−B$^+$ consisting of the neutral atom A interacting with a cation B$^+$. This cation will not, in general, be in the ground state of the B$^+$ system, but if $\mathbf{r}_1$ is actually at a significant distance from the electronic cloud of B$^+$, although still by assumption much closer to B than to A, it has been established by Katriel and Davidson[73] that B$^+$, in that case, tends to its ground state. So in that case at large bond distances $R$(A−B) the energy of this system reduces to

$$E(A-B^+) = E_0(A) + E_0(B) + I_B + E_{\rm int}(A-B^+) \tag{6.13}$$

where $E_0$(A) and $E_0$(B) are the ground state energies of the atoms A and B, respectively. $E_{\rm int}(A-B^+)$ is the energy of interaction of the atom A with the cation B$^+$. If we allow $\mathbf{r}_1$ to be in the neighborhood of the other electrons of B$^+$, it is necessary to take into account that the conditional amplitude will not describe the ground state of B$^+$. The fact that the system described by $\Phi$ is "distorted" will correspond to an energy rise $\Delta E$ with respect to the ground state energy. We may therefore write the energy $E^{N-1}(\mathbf{r}_1 \in \Omega_B)$ in general as

$$E^{N-1}(\mathbf{r}_1 \in \Omega_B) \approx E_0(A) + E_0(B) + I_B + E_{\rm int}(A-B^+) + \Delta E(A-B^+;\mathbf{r}_1) \tag{6.14}$$

If $R$(A−B) is large and $\mathbf{r}_1$ is in the region of the HOMO (*i.e.* not in the subvalence or core region of B), the effect of the electron redistribution incorporated in the last term is expected to be small. Since $I_A < I_B$, the ground state energy $E_0^{N-1}$ of the A−B$^+$ system will correspond for large $R$(A−B) to the system A$^+$−B of the neutral atom B interacting with the cation A$^+$, so that $E_0^{N-1}$ is expressed as

$$E_0^{N-1} \approx E_0(A) + E_0(B) + I_A + E_{\rm int}(A^+-B) \tag{6.15}$$

Inserting (6.15) and (6.14) into (6.12) for $v^{\rm resp}$ yields

$$v^{\rm resp}(\mathbf{r}_1 \in \Omega_B) \approx [I_B - I_A] + [E_{\rm int}(A-B^+) - E_{\rm int}(A^+-B)] + \Delta E(A-B^+;\mathbf{r}_1) \tag{6.16}$$

Suppose now that the reference electron is in the region $\Omega_A$ of the less electronegative atom A, $\mathbf{r}_1 \in \Omega_A$. In this case the conditional amplitude describes the $(N-1)$-electron system A$^+$−B, disturbed around the reference position. If $R$(A−B) is large and $\mathbf{r}_1$ is in the region of the HOMO, this system is close to the ground state of the cation (AB)$^+$. As a result, only the corresponding correction term $\Delta E(A^+-B;\mathbf{r}_1)$ contributes to $v^{\rm resp}(\mathbf{r}_1)$ in this region

$$v^{\rm resp}(\mathbf{r}_1 \in \Omega_A) \approx \Delta E(A^+-B;\mathbf{r}_1) \tag{6.17}$$

From (6.17) and (6.14) we can estimate the up-shift $\Delta v^{\rm resp}$ around the more electronegative atom B

$$\begin{aligned}\Delta v^{\rm resp} &= v^{\rm resp}(\mathbf{r}_1 \in \Omega_B) - v^{\rm resp}(\mathbf{r}_1 \in \Omega_A)\\ &= [I_B - I_A] + [E_{\rm int}(A-B^+) - E_{\rm int}(A^+-B)] +\\ &\qquad [\Delta E(A-B^+;\mathbf{r}_1 \in \Omega_B) - \Delta E(A^+-B;\mathbf{r}_1 \in \Omega_A)]\end{aligned} \tag{6.18}$$

The leading term of (6.18) at large bond distances $R$(A−B) is just the difference of the ionization energies of atoms A and B. This expression demonstrates that the positive buildup $\Delta v_{\rm xc} \approx (I_B - I_A)$ has its origin in the response part $v^{\rm resp}$ of $v_{\rm xc}$ or more precisely in the $v^{N-1}$ component of $v^{\rm resp}$. It is caused by the difference between the conditional amplitude distribution $|\Phi(2...N|1|^2$ of $(N-1)$ electrons and the ground state distribution of the cation (AB)$^+$. When $\mathbf{r}_1 \in \Omega_B$, the conditional amplitude distribution corresponds to the system A−B$^+$, while the ground state is the cation A$^+$−B. Thus, the conditional amplitude, embodying the electron correlation which causes the complete exchange−correlation hole to be located around the reference position, leads to a "repulsive" effect on $v_{\rm xc}$ in $\Omega_B$. The KS potential at a point $\mathbf{r}_1$ in the energetically favorable region around the electronegative atom B is shifted upward by a potential barrier of height $(I_B - I_A)$, which originates from $v^{N-1}$, to prevent a too strong localization of electrons in that region. The terms in the second and third brackets of (6.18) provide corrections to the leading term at large $R$(A−B). The second term represents a correction from the atom-cation interaction, which is different for pairs A$^+$−B and A−B$^+$. The third term represents a difference between the energy effects of the redistribution of $(N-1)$ electrons of A$^+$−B and A−B$^+$ due to the presence of the reference electron position in the outer region of the corresponding charged atom. In other words, the first term brings the main contribution to $\Delta v^{\rm resp}$ due to the different ionization energies of A and B, the second one brings a correction due to the different interaction of A and B with a positive ion, and the third one brings a correction due to the different distortions of the cations A−B$^+$ and A$^+$−B due to different "response" to the proximity of the reference electron position.

All the terms in $\Delta v^{\rm resp}$ (6.18) tend to decrease with decreasing electronegativity difference of atoms A and B, and turn into zero for the homoatomic molecule A$_2$, as they should. For *A*$_2$ the expression

$$v^{\rm resp}(\mathbf{r}_1) = \Delta E(A^+-A;\mathbf{r}_1) \tag{6.19}$$

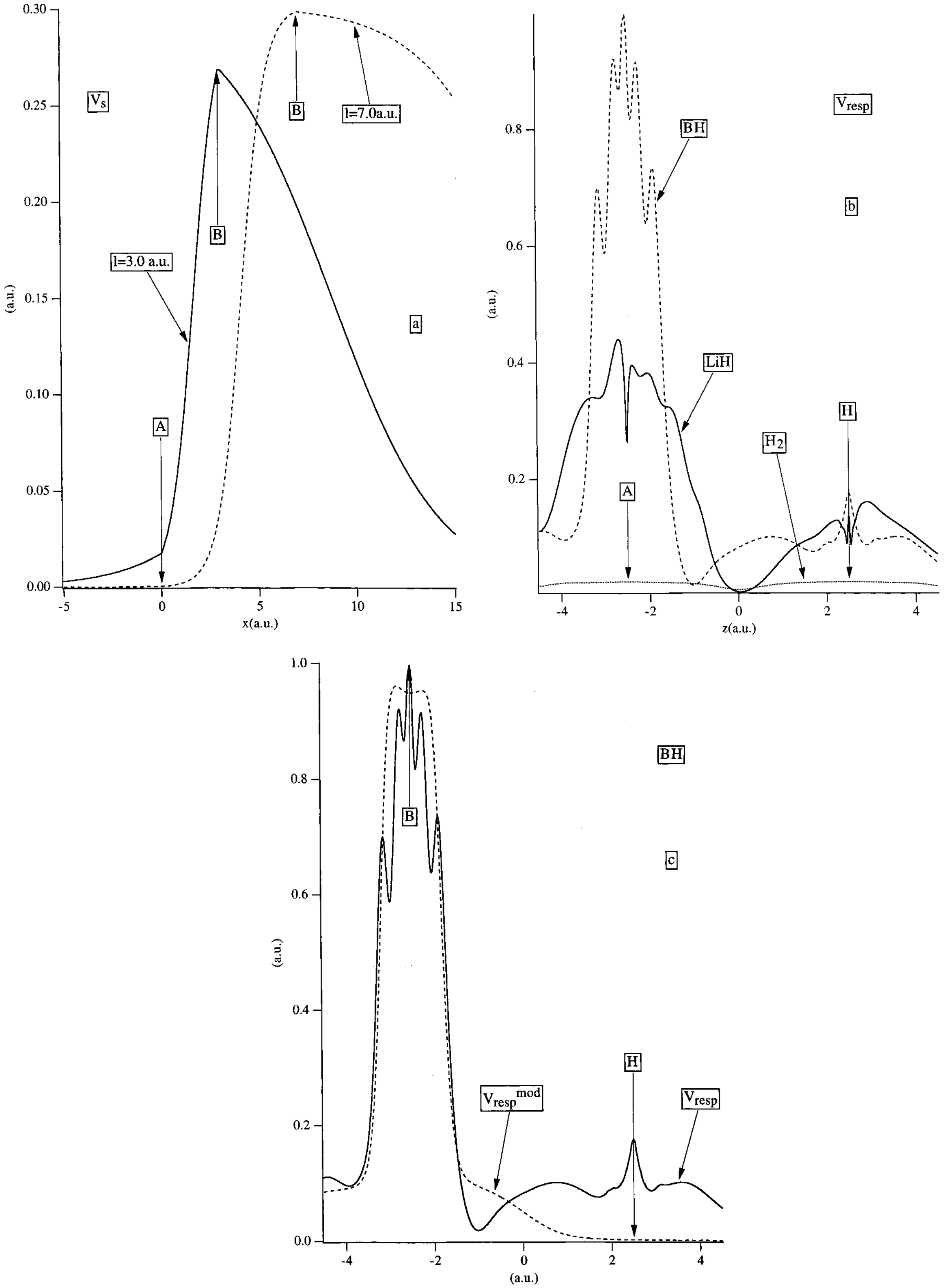

**Figure 6.** (a) Kohn−Sham potential in a model one-dimensional diatomic two-electron molecule AB with ionization potential energy difference $I_B - I_A = 0.302$ au, similar to LiH; (b) response potentials $v^{\mathrm{resp}}$ for $H_2$, LiH, and BH, all at $R = 5.0$ bohr; and (c) response potential $v^{\mathrm{resp}}$ and model response potential for BH at $R = 5.0$ bohr.

which is the analogue of (6.17), is valid for the HOMO region, and $v^{\mathrm{resp}}(\mathbf{r}_1)$ is expected to be small and have a flat form in this region. This is what we have observed for the $H_2$ molecule above.

In Figure 6 we illustrate these points with plots of $v_s$ for a model heteronuclear diatomic molecule (Figure 6a) and for $v^{\mathrm{resp}}$ for LiH, BH, and $H_2$ at the elongated distance of 5.0 bohr (Figure 6b). Following Perdew[133] we construct a model diatomic molecule from two interacting "one-dimensional hydrogen-like atoms". A single electron of the model "atom" is bound to the external delta-function potential $v(x) = - a\delta(x)$, so that the "atomic orbital" is $\phi_A(x) = a^{1/2} \exp(-a|x|)$ and the ionization energy $I_A$ is $a^2/2$. The single KS orbital of the closed-shell system AB is constructed as the bonding orbital

$$\phi(x) = c[\sqrt{a}e^{-a|x|} + \sqrt{b}e^{-b|x-l|}] \tag{6.20}$$

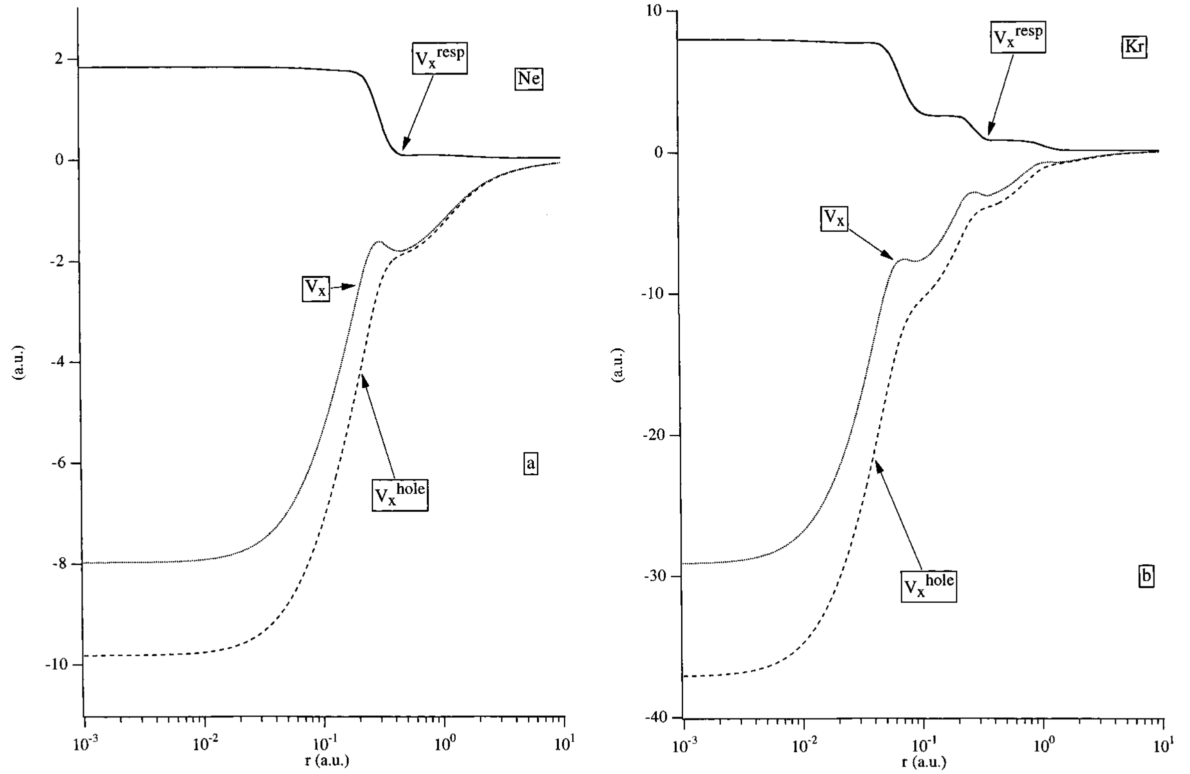

**Figure 7.** Step structure of the response part of the exchange potential in Ne and Kr.

where $l$ is the bond length and $c$ normalizes the total density $\rho(x) = 2|\phi(x)|^2$ to two electrons. At large distance $l$ this construction correctly yields the sum of the "atomic" densities for $\rho(x)$. The energy $\epsilon$ of $\phi(x)$ is equal to minus the ionization energy of the system, which at large $l$ values is equal to that of the less electronegative atom A, $\epsilon = -a^2/2$.

Figure 6a represents the KS potential $v_s(x)$ of the system AB obtained for $l = 3$, $l = 7$ bohr and $x \neq x_A$, $x \neq x_B$ by solving the equation

$$\frac{1}{2}\frac{d^2\phi(x)}{dx^2} + v_s(x)\phi(x) = \epsilon\phi(x) \qquad (6.21)$$

for $v_s(x)$, using $\epsilon = -a^2/2$ and (6.20) for $\phi(x)$. The parameter values $a = 0.63$ and $b = 1.0$ au were chosen in order to fit the ionization energies of the atoms Li and H, respectively. Figure 6a clearly displays the distinct positive buildup of $v_s(x)$ around the more electronegative atom B. In the region between the nuclei $v_s(x)$ has a similar shape for the two distances, stepping up when going from A to B. In the outer region, beyond the B "atom", $v_s(x)$ gradually decreases for $l = 3$ au, forming a rather sharp peak around B. For $l = 7$ au it has a much more shallow form and forms a step with the B atom on its upper part. With increasing $l$ the maximum of $v_s(x)$ approaches the value $I_B - I_A = 0.302$ au.

Figure 6b shows that $v^{resp}$ becomes rather high in the 1$s$ region of Li and B, a feature that will be discussed below, but it also demonstrates that in the region of the H atom $v^{resp}$ stays flat in the case of $H_2$ but clearly builds up in the case of LiH and BH.

We have been discussing the properties of $v^{resp}$ in the region of a valence electron pair, either in an atomic shell such as the 1s shell of He or in a bonding pair in a homonuclear or heteronuclear diatomic molecule. As a last point we wish to mention the strong step-like behavior of $v^{resp}$ when going in an atom from one shell to the next.[78,91,92] In atoms the Fermi correlation is much stronger than the Coulomb correlation, and the step behavior of $v^{resp}$ in atoms is caused by the response part of the exchange potential $v_X$. It already shows up in an exchange-only treatment like the optimized potential model (OPM[135−137]), which seeks to obtain the best local potential to generate orbitals that minimize the energy of a one-determinantal wave function. The local potential contains, apart from the external (nuclear) and electronic Coulomb potentials, an exchange potential $v_X$ that consists of a hole or screening part and a response part,

$$v_x = v_x^{hole} + v_x^{resp} \qquad (6.22)$$

Figure 7 shows plots of the full $v_X$ as well as the hole and response parts for Ne and Kr, which clearly demonstrate the step-like behavior of $v_x^{resp}$. The hole part (or Slater potential[1]) is just the average over the orbital-dependent Hartree−Fock exchange potentials for all occupied orbitals and describes the potential of the Fermi hole,

$$v_{xi}(1) = -\frac{1}{\phi_i^*(1)}\sum_k^N \int f_k \frac{\phi_i^*(2)\phi_k(2)}{r_{12}}\, d2\, \phi_k^*(1)$$

$$v_x^{hole}(1) = \sum_i^N \frac{v_{xi}(1)|\phi_i(1)|^2}{\rho(1)} \qquad (6.23)$$

The exchange response potential

$$v_x^{resp}(1) = \frac{1}{2}\int \frac{\rho(2)\rho(3)}{r_{23}} \frac{\delta g_s(2,3)}{\delta \rho(1)}\, d2\, d3 \qquad (6.24)$$

may be simplified,[92] within certain approximations, to a form first obtained by Krieger, Li, and Iafrate (KLI)[137]

$$v_x^{\mathrm{resp,KLI}}(1) = \sum_i^N w_i \frac{|\phi_i(1)|^2}{\rho(1)} \qquad (6.25)$$

where the weights $w_i$ for each orbital contribution $|\phi_i(1)|^2/\rho(1)$ are the difference of the expectation values over the orbital $\phi_i$ of the full exchange potential $v_x$ and the Hartree−Fock orbital-dependent exchange potential,

$$w_i = \int \phi_i^*(1)[v_x(1) - v_{xi}(1)]\phi_i(1)\, \mathrm{d}1 \qquad (6.26)$$

The form (6.25) of the response potential suggests a step form, since within a given shell the total density will be dominated by the orbital density of that shell, so $|\phi_i(1)|^2/\rho(1)$ will be in the order of 1 and the constants $w_i$ will govern the step heights. Physically the step form of the response potential is related[92] to the "jumping" behavior of the Fermi hole.[100,138] When the reference position moves inside a shell, the shape of the Fermi hole is approximately constant and similar in shape and spatial extent to the shell density—much like we observed in the two-electron case before—but when the reference position crosses the boundary between two shells the hole "jumps" to the shape that corresponds to the new shell. We note that the characteristic little peaks in $v_x$ at the shell boundaries are actually built in by the superposition of the step-like $v_x^{\mathrm{resp}}$ on the much smoother hole potential $v_x^{\mathrm{hole}}$. Modeling of $v_x$ is greatly facilitated by this observation and it has been shown[78] that a satisfactory model response potential is obtained by using the KLI form (6.25) with the weights $w_i$ determined as $K[\rho](\mu - \epsilon_i)^{1/2}$

$$v_x^{\mathrm{resp,mod}}(1) = \sum_i^N K[\rho]\sqrt{\mu - \epsilon_i}\, \frac{|\phi_i(1)|^2}{\rho(1)} \qquad (6.27)$$

This form of the response potential obeys requirements like gauge invariance and proper scaling of $v_x$ and $\epsilon_i$

$$v_x([\rho];\mathbf{r}) = \lambda v_x([\rho];\lambda\mathbf{r}) \qquad (6.28)$$

$$\epsilon_i[\rho_\lambda] = \lambda^2 \epsilon_i[\rho] \qquad (6.29)$$

upon scaling of the density

$$\rho_\lambda(\mathbf{r}) = \lambda^3 \rho(\lambda\mathbf{r}) \qquad (6.30)$$

Expression (6.27) becomes exact for the homogeneous electron gas with

$$K = \frac{8\sqrt{2}}{3\pi^2} \approx 0.382 \qquad (6.31)$$

Figure 6c shows for BH at 5.0 bohr that this model response potential does describe the high step in the 1s region of B and also the weaker "step" in the 2s region, but it fails to describe the positive build up around H.

## 7. Summary

The central tenet in this discussion of DFT has been the role of the Kohn−Sham one-electron model as an alternative molecular orbital theory to be clearly distinguished from Hartree−Fock. It does not, as some semiempirical methods do, strive to mimick Hartree−Fock as closely as possible, but it is related to the exact solution of the many-electron problem. We have highlighted the difference between the Kohn−Sham and Hartree−Fock models. In particular we have stressed that the correlation energy is defined in DFT in a different way than traditionally in quantum chemistry. It is the difference between the exact total energy and the energy of the Kohn−Sham determinantal wave function built from the Kohn−Sham orbitals. Since the latter is necessarily higher than the Hartree−Fock energy, the correlation energy of DFT will be larger (more negative) than the traditional one. More importantly, however, it will have very different components, the correlation correction to the electron−nuclear potential energy for instance being zero since the Kohn−Sham density is equal to the exact density. Physically the difference between the Kohn−Sham and Hartree−Fock models may be understood from the fact that the Hartree−Fock "potential" only embodies the Fermi correlation, while the leading term in the Kohn−Sham potential $v_{xc}$ is the potential of the full correlation hole, Fermi plus Coulomb. We have demonstrated that the fact that the effective potential of the Kohn−Sham model incorporates the Coulomb correlation effects is very important for the building of the correct electronic charge distribution. The Kohn−Sham orbitals are physically sound and may be expected to be more suitable for use in qualitative molecular orbital theory than either Hartree−Fock or semiempirical orbitals.

A decomposition of both the exchange−correlation energy density $\epsilon_{xc}$ and the exchange−correlation potential $v_{xc}$ has demonstrated that these quantities may be related directly to various aspects of electron correlation. The most important term in both is the potential of the Fermi plus Coulomb hole, $v_{xc}^{\mathrm{hole}}$. Both also contain a kinetic correlation potential $v_{c,\mathrm{kin}}$, accounting for the difference $T_c$ between the exact kinetic energy and the kinetic energy $T_s$ of the Kohn−Sham orbitals. Whereas $v_{xc}^{\mathrm{hole}}$ gives in a sense a static picture of the correlation, reflecting the shape of the total hole around the reference position, $v_{c,\mathrm{kin}}$ in a sense reflects a dynamic aspect of correlation, being sensitive to the rate of change of the total hole when the reference position changes. This is particularly relevant around the bond midpoint, where the Coulomb hole, being localized around the nucleus close to the reference position, rapidly switches from one nucleus to the other one. There is in $v_{xc}$ (but not in $\epsilon_{xc}$) a third term, the response part of the Kohn−Sham potential. Special features of $v^{\mathrm{resp}}$, such as its typical step behavior in atoms when going from one shell to the next and the positive buildup around the most electronegative nucleus in a heteronuclear molecule, have been related to the electron correlation by using an expression for $v^{\mathrm{resp}}$ in terms of the conditional amplitudes $\Phi(2...N\,|\,1)$ and $\Phi_s(2...N\,|\,1)$ of the exact interacting system and the Kohn−Sham system, respectively.

We finally note that the special properties of the Kohn−Sham orbitals also make the KS determinant an interesting zero-order approximate wave function. Although the KS determinant lacks certain convenient properties of the HF determinant, it may be well worth studying CI and perturbation treatments in the KS orbital basis.

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