Analysis of correlation in terms of exact local potentials:
Applications to two-electron systems

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For a two-electron system the Kohn-Sham potential of density-functional theory is equal to the effective local potential $V_{eff}(x_1)$ occurring in the one-electron Schrödinger equation that is satisfied by the square root of the exact many-electron density, $\rho^{1/2}(x_1)$. Making use of the theory of marginal and conditional probability amplitudes, it is shown that $V_{eff}(x_1)$ is the sum of three potentials, each of which has a clear physical interpretation and will be studied in detail. The correlation part of the Kohn-Sham potential in a two-electron system can then be obtained by subtraction of the Coulomb and exchange potential, and it is shown how we can express this correlation potential as the sum of three physically meaningful contributions. The connection between the Kohn-Sham potential in a many-electron system and V_{eff} is also discussed. Calculations of the various potentials from highly accurate configuration-interaction wave functions are presented for the helium atom and for the hydrogen molecule at various distances of the two hydrogen nuclei.

I. INTRODUCTION

The local one-electron Kohn-Sham potential of density-functional (DF) theory[1,2] is of great potential utility for the description of complex electronic systems in that it offers a simple route to obtaining the exact ground-state density and ultimately, it is hoped, the total energy. The exchange-correlation part of the total energy, E_{xc} depends on the density through a universal but unknown functional $E_{xc}[\rho]$, as was proven by Hohenberg and Kohn.[2] The Kohn-Sham (KS) potential is, apart from a Coulomb term, equal to the functional derivative of E_{xc} with respect to the density[1]

$$V^{KS}(x_1) = \int [\rho(x_2)/r_{12}]dx_2 + \delta E_{xc}[\rho]/\delta\rho .$$

Considerable effort is currently being spent to model the unknown functional E_{xc} or the related exchange-correlation potential. An analysis of accurate correlated potentials, calculated from nearly exact wave functions, should lead to a better understanding of the correlation-potential relationship, which may prove to be very helpful in the search for good model potentials. However, in DF theory exact relationships between ground-state wave functions and their corresponding exchange-correlation potentials have been nonexistent. So the exact KS potential cannot be studied simply because it cannot be calculated, not even if the exact wave function is known. An important exception is two-electron systems, where there is only one occupied Kohn-Sham orbital, equal to $\rho^{1/2}/\sqrt{2}$, and V^{KS} is equal to V_{eff}, the effective one-electron potential that occurs in the Schrödinger-like differential equation that is satisfied by the square root of the *exact* ground-state density $\rho(x_1)$:[3−6]

$$[-\tfrac{1}{2}\nabla_1^2 + V_N(x_1) + V_{eff}(x_1)]\rho^{1/2}(x_1) = \varepsilon\rho^{1/2}(x_1) , \quad (1)$$

where $V_N(x_1)$ is the external (usually the electron-nuclear) potential. For this reason we will, in this article, calculate and analyze V_{eff}, and therefore V^{KS} for two-electron systems using Eq. (3) below. The relation between the Kohn-Sham potential and V_{eff} in systems with more than two electrons will be analyzed in a similar way, cf. Eqs. (4) and (5) below.

Hunter derived Eq. (1) within the theory of conditional and marginal probability amplitudes[7] and subsequently used V_{eff} for the interpretation of the electronic structure of some small molecules [on the Hartree-Fock (HF) level].[3] He showed that the total potential in (1) can be expressed as an expectation value

$$V_N(x_1) + V_{eff}(x_1) = \int \Phi^*(x_2 \cdots x_N | x_1)$$
$$\times H^N\Phi(x_2 \cdots n_N | x_1)dx_2 \cdots dx_N ,$$
$$(2)$$

where H^N is the full N-electron Hamiltonian and the "wave function" Φ, called the conditional amplitude, is the amplitude related to the probability distribution of the $N-1$ electrons associated with positions $x_2..x_N$, when one electron is known to be at position x_1. The wave-function–potential relationship (2) was noted (and used) by several other authors, looking at Eq. (1) from different perspectives.[4−6] It not only creates the possibility to calculate V_{eff} directly from the wave function, but it also enables one to prove and understand various aspects of V_{eff}. For instance, Levy, Perdew, and Sahni[4] proved that $V_{eff}(x_1) \geq 0$ for all x_1 and that (for atoms) $V_{eff}(r)$ decays like $(N-1)/r$ in the limit $r \to \infty$. They also showed that the eigenvalue ε in (1) is equal to the negative of the ionization potential $\varepsilon = E_0^N - E_0^{N-1}$.

In this article we will further analyze the effective potential with the purpose of obtaining a better insight into the nature of the relationship between correlation and the

potential. We will show that each of the three contributions that arise naturally in the derivation of (2) has a clear physical interpretation

$$V_{\text{eff}}(x_1) = V_{\text{cond}}(x_1) + V_{\text{kin}}(x_1) + V^{N-1}(x_1) . \tag{3}$$

The first term $V_{\text{cond}}(x_1)$ is the conditional potential; it is the exact average repulsion that an electron at position x_1 experiences from the other $N-1$ electrons in the system. This potential is different from the average Hartree-Fock potential primarily in that it incorporates the effect of Coulomb correlation (the Coulomb hole in addition to the Fermi hole). The second term $V_{\text{kin}}(x_1)$ is a correction accounting for the difference in kinetic energy density between an electron in the orbital $N^{-1/2}\rho^{1/2}(x_1)$ and an electron in a "real" N-electron system. The last term $V^{N-1}(x_1)$ is the (x_1-dependent) total energy (kinetic plus potential) of the system of $N-1$ electrons that are described by the conditional amplitude Φ (parametrically dependent on x_1) minus the ground-state energy of the $N-1$ electron system. Because of the quite different origin and nature of these three contributing potentials, studying them individually is probably more illuminating than to study their sum, the total effective potential.

In a many-electron or extended system the effective potential will not be equal to the KS potential. There is, however, a close connection between the two, as was noted by several authors:[8,9]

$$V^{\text{KS}} = V_{\text{eff}} - V_{\text{Pauli}} . \tag{4}$$

The so-called Pauli potential is defined as the functional derivative of the difference between the Kohn-Sham kinetic energy $T_s[\rho]$ and the full von Weizsäcker kinetic energy $T_W[\rho]$. As mentioned before, this difference, and therefore also V_{Pauli}, is zero in the case of a two-electron system. In a recent article Levy and Ou-Yang studied this Pauli potential in detail.[8] We will show that we can write V_{Pauli} in terms of contributions similar to the ones that enter Eq. (2),

$$V_{\text{Pauli}} = V_{\text{kin}}^{\text{KS}} + V^{\text{KS},N-1} , \tag{5}$$

and that the KS potential can be expressed as

$$V^{\text{KS}} = V_{\text{cond}} + (V_{\text{kin}} - V_{\text{kin}}^{KS}) + (V^{N-1} - V^{\text{KS},N-1}) . \tag{6}$$

The two terms $V_{\text{kin}}^{\text{KS}}$ and $V^{\text{KS},N-1}$ can be calculated from the KS wave function, defined as the one-determinantal wave function containing the Kohn-Sham orbitals, in precisely the same way as V_{kin} and V^{N-1} are calculated from the exact wave function.

It is customary to distinguish Coulomb, exchange, and correlation contributions to V^{KS}:

$$V^{\text{KS}}(x_1) = V_{\text{Coulomb}}(x_1) + V_x(x_1) + V_{\text{corr}}^{\text{KS}}(x_1)$$
$$= V^{\text{HF}}(x_1) + V_{\text{corr}}^{\text{KS}}(x_1) . \tag{7}$$

There is an ambiguity in the definition of V_{Coulomb} and V_x and therefore in $V_{\text{corr}}^{\text{KS}}$. The Coulomb and exchange potentials may be obtained from exact densities (c.q., density matrices), or they may refer to Hartree-Fock densities.

If necessary, we distinguish by writing $V^{\text{HF}}(\rho^{\text{HF}})$ or $V^{\text{HF}}(\rho^{\text{exact}})$. Using Eq. (3) we have, for two-electron systems ($V_{\text{eff}} = V^{\text{KS}}$),

$$V_{\text{corr}}^{\text{KS}}(x_1) = [V_{\text{cond}}(x_1) - V^{\text{HF}}(x_1)]$$
$$+ V_{\text{kin}}(x_1) + V^{N-1}(x_1) . \tag{8}$$

This expression displays explicitly three physically meaningful contributions to $V_{\text{corr}}^{\text{KS}}$. These will be the main focus of this paper.

It has been recognized, of course, that the calculation of (almost) exact effective potentials from accurate correlated ground-state wave functions for a number of systems, making use of the wave-function–potential relationship (2), may prove very helpful in the current search for good model potentials. However, calculations of accurate Kohn-Sham potentials have been published for a few light atoms only (the He isoelectronic series, Li, and Be),[10,11] and never for a molecule. In these calculations numerical techniques were used to obtain the potential from an accurate density, e.g., transformation of Eq. (1) into an equation for $V_{\text{eff}}(x_1)$.[10] But these numerical methods only give the shape of $V_{\text{eff}}(x_1)$; in particular, they do not clarify the structure of $V_{\text{eff}}(x_1)$ in terms of wave-function expectation values as in (3). Hunter and Tai[12] calculated the total effective potential in (2) from a (essentially exact) ten-term Hylleraas wave function for the He ground state and compared this potential with effective potentials obtained from approximate wave functions. However, they did not analyze the potential in terms of the various components that build $V_{\text{eff}}(x_1)$ in Eq. (3). Such an analysis will be carried out in this paper for He and H_2 at various bond distances.

The organization of the paper is as follows. In Sec. II we will derive an expression for the effective potential directly from the Schrödinger equation. We will show how this potential comes out naturally as the sum of the three potentials in (3) and we will interpret these potentials in detail. Also, a connection is made with propagator theory. In Sec. III we report on calculations of the effective potential for the He atom and for the H_2 molecule at various distances of the two hydrogen nuclei. Because He and H_2 are two-electron systems, the effective potential is the same as the total effective Kohn-Sham potential.

H_2 is an interesting system for several reasons. We can demonstrate and study the behavior of the effective and KS potential in the bonding region and by changing the internuclear distance we can analyze the effect of bond formation or bond breaking. The H_2 molecule is also a classical example for which the Hartree-Fock model breaks down at large internuclear distances. While in H_2 at equilibrium distance (and also in the helium atom) the effective potential is expected to resemble the HF potential, as in those cases the HF model is fairly accurate, the effective potential may differ from the HF potential considerably at large internuclear distances. This will allow us to study the effects of correlation on the effective potential and its components in precisely the interesting case where they become large.

II. THEORY AND METHOD

In this section we will derive an expression for the effective local potential $V_{\text{eff}}(x_1)$ directly from the N-electron Schrödinger equation. Although we limit ourselves to ground-state wave functions and densities, it is not necessary to do so. The derivation is valid for any exact eigenstate of the N-electron Hamiltonian. It is only if we want to identify the effective potential with the total Kohn-Sham potential (in two-electron systems) that we must return to the ground state because the Kohn-Sham potential is defined for the ground state only.

In 1975 Hunter developed the theory of the conditional probability amplitudes.[7] In this theory the wave function Ψ is expressed as a product of a marginal and a conditional amplitude

$$\Psi(x_1 \cdots x_N) = f(x_1)\Phi(x_2 \cdots x_N | x_1) . \qquad (9)$$

The conditional amplitude $\Phi(x_2 \cdots x_N | x_1)$ describes the system of the $N-1$ electrons with positions $x_2 \cdots x_N$, when one electron is known to be at position x_1. It plays a key role in the subsequent development, and in the expressions for the potentials of Eq. (3) [cf. Eqs. (28)–(30).] If we require the conditional amplitude to be normalized,

$$\int \Phi^*(x_2 \cdots x_N | x_1)\Phi(x_2 \cdots x_N | x_1) dx_2 \cdots dx_N = 1$$

$$\text{for all } x_1 , \qquad (10)$$

then the square of the marginal amplitude is determined by

$$|f(x_1)|^2 = \int \Psi^*(x_1 \cdots x_N)\Psi(x_1 \cdots x_N) dx_2 \cdots dx_N$$

$$= N^{-1}\rho(x_1) . \qquad (11)$$

Because $\rho(x_1)$ is, in general, a nodeless function, we can choose $f(x_1)$ to be the positive square root of the density

$$f(x_1) = N^{-1/2}\rho^{1/2}(x_1) . \qquad (12)$$

The one-particle density associated with the conditional amplitude is called the conditional density

$$\rho^c(x_2 | x_1) = (N-1)\int \Phi^*(x_2 \cdots x_N | x_1)$$

$$\times \Phi(x_2 \cdots x_N | x_1) dx_3 \cdots dx_N$$

$$= \Gamma^{(2)}(x_1, x_2)/\rho(x_1) , \qquad (13)$$

where $\Gamma^{(2)}(x_1, x_2)$ is (the diagonal part of) the two-particle density matrix associated with Ψ.

Let $\Psi_0(x_1 \cdots x_N)$ be an exact N-electron ground-state wave function

$$H^N\Psi_0 = E_0^N\Psi_0 . \qquad (14)$$

We now partition the N-electron Hamiltonian H^N as

$$H^N = H^{N-1} + \sum_{p>1} 1/r_{1p} + V_N(x_1) - \tfrac{1}{2}\nabla_1^2 , \qquad (15)$$

and we get, writing Ψ_0 in the product form (9),

$$\left[H^{N-1} + \sum_{p>1} 1/r_{1p} + V_N(x_1) - \tfrac{1}{2}\nabla_1^2 \right]$$

$$\times f(x_1)\Phi(x_2 \cdots x_N | x_1) = E_0^N f(x_1)\Phi(x_2 \cdots x_N | x_1) . \qquad (16)$$

Now multiply both sides by $\Phi^*(x_2 \cdots x_N | x_1)$ and integrate over the coordinates $x_2 \cdots x_N$. Making use of the normalization requirement (10), we get, writing Φ for $\Phi(x_2 \cdots x_N | x_1)$,

$$f(x_1)\int \Phi^* H^{N-1}\Phi dx_2 \cdots dx_N$$

$$+ f(x_1)\sum_{p>1} \int \Phi^* \frac{1}{r_{1p}}\Phi dx_2 \cdots dx_N + V_N(x_1)f(x_1)$$

$$+ \int \Phi^*(-\tfrac{1}{2}\nabla_1^2)f(x_1)\Phi dx_2 \cdots dx_N = E_0^N f(x_1) . \qquad (17)$$

Equation (17) is a one-electron Schrödinger-like equation, satisfied by the orbital $f(x_1)$. To show this more clearly we simplify and interpret the various terms in (17) and reach an expression for the effective potential.

The first term on the left-hand side (LHS) of (17) is $f(x_1)$ times the energy expectation value of the system of $N-1$ electrons described by the conditional amplitude $\Phi(x_2 \cdots x_N | x_1)$. This energy expectation value is parametrically dependent on x_1, the position of the reference electron. It is this term that determines the value of the effective potential in the limit $x_1 \to \infty$. In an interesting paper, Katriel and Davidson proved[13] that the conditional amplitude Φ, if calculated from the exact ground-state N-electron function Ψ_0^N, becomes equal to the exact ground-state function of the $N-1$ electron system if $x_1 \to \infty$. Consequently, the first term on the LHS of (17) is, in this limit, equal to $f(x_1)$ times E_0^{N-1}, the ground-state energy of the $N-1$ electron system. If we require the effective potential to approach zero in the limit $x_1 \to \infty$ we must subtract $f(x_1)$ times E_0^{N-1} from both sides in Eq. (17). The potential obtained in this way will be denoted $V^{N-1}(x_1)$:

$$V^{N-1}(x_1) = \int \Phi^* H^{N-1}\Phi dx_2 \cdots dx_N - E_0^{N-1} . \qquad (18)$$

We note that this potential is positive for all positions of x_1. Its value at general positions x_1 depends on the details of the correlation embodied in the conditional amplitude Φ. It is, however, interesting to observe that taking the expectation value of the potential $\int \Phi^* H^{N-1}\Phi dx_2 \cdots dx_N$ for the one-electron wave function $f(x_1)$, which is equivalent to taking the expectation value of H^{N-1} for the complete wave function Ψ, gives the total energy of the N-electron system minus the (average) energy associated with one electron, i.e., $1/N$-th of the total kinetic and nuclear attraction energies (E_K and E_{Ne}, respectively) and $N-1$ pair repulsion energies $E_{ee}/[N(N-1)/2]$,

$$\left\langle f(x_1) \left| \int \Phi^* H^{N-1}\Phi dx_2 \cdots dx_N \right| f(x_1) \right\rangle$$

$$= E_0^N - \frac{1}{N}E_K - \frac{1}{N}E_{Ne} - \frac{2}{N}E_{ee} . \qquad (19)$$

This will be demonstrated explicitly below [see Eq. (33)].

Using (13), the second term on the LHS of (17) can be written as

$$f(x_1)\sum_{p>1}\int \Phi^* \frac{1}{r_{1p}}\Phi dx_2 \cdots dx_N = f(x_1)\int \frac{\rho^c(x_2|x_1)}{r_{12}}dx_2$$

$$= f(x_1)V_{\text{cond}}(x_1) , \quad (20)$$

where $V_{\text{cond}}(x_1)$, the conditional potential, is the average repulsion that an electron at position x_1 experiences from the other $N-1$ electrons in the system. It is the major part of the total effective potential V_{eff}. In 1953 Slater[14] discussed this potential and argued that it is to be preferred in one-electron calculations over the Hartree-Fock potential. In the limit $x_1 \rightarrow \infty$, $V_{\text{cond}}(x_1)$ decays like $(N-1)/r$. Since this is also the decay rate of the total effective potential $V_{\text{eff}}(x_1)$, as demonstrated by Levy, Perdew, and Sahni,[4] the other terms in $V_{\text{eff}}(x_1)$ vanish more rapidly than $(N-1)/r$ in this limit.

To simplify the fourth term on the LHS of (17) we first write down an expression for the density matrix,

$$\gamma(x_1',x_1) = N\int \Psi_0^*(x_1' \cdots x_N)\Psi_0(x_1 \cdots x_N)dx_2 \cdots dx_N$$

$$= Nf(x_1')f(x_1)G(x_1',x_1) . \quad (21)$$

This equation defines the function $G(x_1',x_1)$, which we can also write as

$$G(x_1',x_1) = \int \Phi^*(x_2 \cdots x_N|x_1')$$

$$\times \Phi(x_2 \cdots x_N|x_1)dx_2 \cdots dx_N . \quad (22)$$

The function $G(x_1',x_1)$ is the overlap between two conditional amplitudes, with the reference electron at positions x_1' and x_1, respectively. From (21) and (22) it is easy to derive the result $G(x_1,x_1)=1$ and $\nabla_1 G(x_1',x_1)|_{1'=1}=0$.

Because $f(x_1)$ is equal to the square root of the diagonal density $\rho(x_1) \equiv \gamma(x_1,x_1)$, we see from (21) that all the off-diagonal density-matrix information ends up in the G function. In a Hartree-Fock system G describes exchange effects only. The Hartree-Fock two-electron density matrix,

$$\Gamma^{(2)HF}(x_1,x_2) = \gamma^{HF}(x_1,x_1)\gamma^{HF}(x_2,x_2) - \gamma^{HF}(x_1,x_2)\gamma^{HF}(x_2,x_1)$$

$$= \rho^{HF}(x_1)\rho^{HF}(x_2) - \rho^{HF}(x_1)\rho^{HF}(x_2)G^{HF}(x_1,x_2)G^{HF}(x_2,x_1) , \quad (23)$$

leads to an expression for the conditional density in the Hartree-Fock approximation,

$$\rho^{cHF}(x_2|x_1) = \Gamma^{(2)HF}(x_1,x_2)/\rho^{HF}(x_1)$$

$$= \rho^{HF}(x_2) - \rho^{HF}(x_2)G^{HF}(x_1,x_2)G^{HF}(x_2,x_1)$$

$$\equiv \rho^{HF}(x_2) + \rho^x(x_2|x_1) , \quad (24)$$

which defines the exchange or Fermi hole, with the reference electron at position x_1, as $\rho^x(x_2|x_1) = -\rho^{HF}(x_2)|G^{HF}(x_1,x_2)|^2$. The Fermi hole is evidently definite negative. If we go beyond the HF approximation the exact G will differ from G^{HF} due to correlation. The expression $-\rho(x_2)|G(x_1,x_1)|^2$ is a possible definition of the exchange hole in the case of a correlated wave function.

Using Eqs. (9) and (21) we can rewrite the fourth term on the LHS of (17) as

$$\int \Phi^*(-\tfrac{1}{2}\nabla_1^2)f(x_1)\Phi dx_2 \cdots dx_N$$

$$= N^{-1}f^{-1}(x_1)(-\tfrac{1}{2}\nabla_1^2)\gamma(x_1',x_1)|_{1'=1}$$

$$= \{-\tfrac{1}{2}\nabla_1^2 - [\tfrac{1}{2}\nabla_1^2 G(x_1',x_1)|_{1'=1}]\}f(x_1)$$

$$= [-\tfrac{1}{2}\nabla_1^2 + V_{\text{kin}}(x_1)]f(x_1) . \quad (25)$$

The conditional amplitude Φ depends on the reference position x_1. The average *rate* of change of Φ, given by the potential

$$V_{\text{kin}}(x_1) = \int \Phi^*(-\tfrac{1}{2}\nabla_1^2)\Phi dx_2 \cdots dx_N$$

$$= +\tfrac{1}{2}\int |\nabla_1\Phi|^2 dx_2 \cdots dx_N ,$$

can be interpreted as a measure of how strongly the

motion of an electron at position x_1 is correlated with the other electrons in the system, in the sense that it reflects the magnitude of the change in the conditional amplitude Φ with changing reference position x_1. For instance, in the limit $x_1 \rightarrow \infty$ the conditional amplitude will become independent of x_1 and $V_{\text{kin}}(x_1)=0$. Another region where the correlation of the reference electron with the other electrons in the system becomes independent of the position x_1 is the near neighborhood of a nucleus. Here the electron moves in a potential that is dominated by the field of the nucleus. Intuitively, one expects the (correlated) probability distribution of the other electrons to be almost independent of the position of the reference electron. That indeed $\nabla_1\Phi=0$ and therefore $V_{\text{kin}}(x_1)=0$, if x_1 is at a nucleus, can be derived rigorously from the electron-nuclear cusp conditions for the (exact) wave function.[15] The derivation is given in the Appendix.

A third example of the connection between V_{kin} and the rate of change of the conditional amplitude is provided by the recent investigation of V_{kin} for Hartree-Fock wave functions of atoms by Sierraalta and Ludena.[16] In the HF case we have only exchange correlation, as a result of the antisymmetry of the wave function, and G^{HF} describes the exchange hole only. It has been observed on several occasions[17-20] that the shape of the exchange hole in atoms is relatively insensitive to the position of the reference electron when it moves within one atomic shell. The hole function "jumps," however, to the one appropriate to the next shell if the reference electron moves over to that shell. From the interpretation of V_{kin} given here we would then expect $V_{\text{kin}}^{HF}(x_1)$ to be small for x_1 within a shell and significant when x_1 is in an inter-

shell region. This is precisely what Sierraalta and Ludena observed in their plots of

$$V_{\text{kin}}^{\text{HF}}(x_1) = \tfrac{1}{2}\nabla_1 \cdot \nabla_{1'} G^{\text{HF}}(x_1, x_{1'})|_{1'=1}$$

for rare-gas atoms.[16]

From Eq. (25) we see how the kinetic energy density can be expressed as a sum of the kinetic energy density of the orbital $f(x_1)$ and a correction term

$$(-\tfrac{1}{2}\nabla_1^2)\gamma(x_1', x_1)|_{1'=1} = Nf(x_1)(-\tfrac{1}{2}\nabla_1^2)f(x_1)$$
$$+ V_{\text{kin}}(x_1)Nf(x_1)f(x_1) . \quad (26)$$

In DF theory, the kinetic energy is sometimes written as the functional $T[\rho] = T_W[\rho] + T_{\text{xc}}[\rho]$. The first term in this expression is the traditional Weizsäcker term, a functional of the diagonal density ρ given by $T_W[\rho] = \int [(\nabla\rho)^2/8\rho]d\tau$. Now $T_W[\rho]$ is equal to the energy associated with the first term on the right-hand side (RHS) of (26). The kinetic energy correction, coming from the second term in (26), can be identified with the exchange-correlation energy

$$T_{\text{xc}}[\rho] = \int \rho(x_1)V_{\text{kin}}(x_1)dx_1 .$$

From the fact that the function $G(x_1', x_1)$ has a maximum of 1 in the point $x_1' = x_1$ we can deduce that $V_{\text{kin}}(x_1) \geq 0$ for all x_1. It follows that $T_{\text{xc}}[\rho]$ always makes a positive contribution to the total kinetic energy.[21]

Hartree-Fock theory often does very well in describing the diagonal part of the density matrix. As a consequence, the change in kinetic energy, when going from the HF approximation to exact, will mainly be due to a change in the off-diagonal part of $\gamma(x_1', x_1)$. In atoms and molecules at equilibrium geometry, where the virial theorem (almost) holds for both the HF and the exact case, this kinetic energy difference is about equal to minus the total correlation energy. This means that, in contrast to the diagonal density $\rho(x_1)$, the off-diagonal part of $\gamma(x_1', x_1)$ is not well described by HF theory. It is, therefore, interesting to study the changes in the function $G(x_1', x_1)$ when correlation is introduced.

After carrying through the various simplifications, we can rewrite Eq. (17)

$$[-\tfrac{1}{2}\nabla_1^2 + V_N(x_1) + V_{\text{cond}}(x_1) + V_{\text{kin}}(x_1)$$
$$+ V^{N-1}(x_1)]f(x_1) = \varepsilon f(x_1) , \quad (27)$$

where

$$V_{\text{cond}}(x_1) = \int \Phi^*(x_2 \cdots x_N | x_1) \left[\sum_{p>1} \frac{1}{r_{1p}} \right]$$
$$\times \Phi(x_2 \cdots x_N | x_1)dx_2 \cdots dx_N$$
$$= \int \frac{\rho^c(x_2|x_1)}{r_{12}}dx_2 , \quad (28)$$

$$V_{\text{kin}}(x_1) = \int \Phi^*(x_2 \cdots x_N | x_1)(-\tfrac{1}{2}\nabla_1^2)$$
$$\times \Phi(x_2 \cdots x_N | x_1)dx_2 \cdots dx_N$$
$$= +\tfrac{1}{2}\int |\nabla_1 \Phi|^2 dx_2 \cdots dx_N$$
$$= -\tfrac{1}{2}\nabla_1^2 G(x_1', x_1)|_{1'=1} , \quad (29)$$

$$V^{N-1}(x_1) = \int \Phi^*(x_2 \cdots x_N | x_1)H^{N-1}$$
$$\times \Phi(x_2 \cdots x_N | x_1)dx_2 \cdots dx_N - E_0^{N-1} , \quad (30)$$

$$\varepsilon = E_0^N - E_0^{N-1} , \quad (31)$$

and

$$V_{\text{eff}}(x_1) = V_{\text{cond}}(x_1) + V_{\text{kin}}(x_1) + V^{N-1}(x_1) . \quad (32)$$

The eigenvalue ε, which is the negative of the first ionization potential, in the one-electron Schrödinger equation (27) can be expressed as a sum of orbital expectation values

$$\varepsilon = \langle f| -\tfrac{1}{2}\nabla^2 + V_{\text{kin}}|f\rangle + \langle f|V_N|f\rangle$$
$$+ \langle f|V_{\text{cond}}|f\rangle + \langle f|V^{N-1}|f\rangle$$
$$= (1/N)E_k + (1/N)E_{Ne} + (2/N)E_{ee}$$
$$+ \langle f|V^{N-1}|f\rangle . \quad (33)$$

where E_K, E_{Ne}, and E_{ee} are the total kinetic energy, electron-nuclear attraction energy, and electron repulsion energy of the N-electron system. Now the sum of the first three terms on the RHS of (33) is just the negative of the ionization energy that would be obtained if removing one electron were equivalent to removing $1/N$th of the kinetic and nuclear attraction energy and $N-1$ pair interaction energies. The difference $\langle f|V^{N-1}|f\rangle$ between this "average" ionization energy and the true first ionization potential of course incorporates relaxation effects in the ion which make its average kinetic, nuclear attraction, and pair repulsion energies different from those in the neutral molecule.

At this point it is interesting to note that we can express $V^{N-1}(x_1)$ and also $V_{\text{cond}}(x_1)$ in a different way and make contact with propagator theory. First write the ground-state N-electron function as

$$\Psi_0^N(x_1 \cdots x_N) = N^{-1/2}\sum_i g_i(x_1)\Psi_i^{N-1}(x_2 \cdots x_N) . \quad (34)$$

The Ψ_i^{N-1} are eigenfunctions of H^{N-1} and the g_i are the so-called Dyson orbitals.

By making use of (9), (30), and (34) we can write

$$\rho(x_1)V^{N-1}(x_1) = \sum_{i,j} g_i^*(x_1)g_j(x_1) \int \Psi_i^{N-1*} H^{N-1} \Psi_j^{N-1} dx_2 \cdots dx_N - \rho(x_1)E_0^{N-1}$$

$$= \sum_i |g_i(x_1)|^2 E_i^{N-1} - \rho(x_1)E_0^{N-1} = \frac{1}{2\pi i} \int_c (\varepsilon - \omega)G(x_1,x_1,\omega)d\omega \ . \tag{35}$$

The function $G(x_1',x_1,\omega)$ is the Fourier transform of the one-particle propagator (c is a contour enclosing all ionization poles of G). After some algebraic manipulation of Eqs. (27) and (35), and making use of the density-matrix equation $\gamma(x_1',x_1) = \sum_i g_i(x_1')g_i(x_1)$, we reach an expression for $V_{cond}(x_1)$,

$$\rho(x_1)V_{cond}(x_1) = -h(1)\gamma(x_1',x_1)|_{1'=1} + \sum_i |g_i(x_1)|^2 \varepsilon_i$$

$$= \frac{1}{2\pi i} \int_c (\omega - h)G(x_1,x_1,\omega)d\omega \ , \tag{36}$$

with $h(1) = -\frac{1}{2}\nabla_1^2 + V_N(x_1)$ and $\varepsilon_i = E_0^N - E_i^{N-1}$.

Equations (35) and (36) are interesting because they show how the potentials $V^{N-1}(x_1)$ and $V_{cond}(x_1)$, which both contain correlation information, can be calculated directly from the Dyson orbitals and ionization energies. Recently, Holleboom *et al.* showed how to calculate $V_{cond}(x_1)$ within the Green's-function formalism,[22] and they proposed an approximation method for the one-particle propagator, making use of this potential.[23]

There is a close connection between the effective potential and the total Kohn-Sham potential, as was shown by several authors.[8,9] In the terminology of this section, we can illustrate this most clearly by deriving an expression for V_{eff}, not from the Schrödinger equation, Eq. (14), but from the KS equation $H^{KS}\Psi^{KS} = E^{KS}\Psi^{KS}$, where H^{KS} is the total KS Hamiltonian given by $H^{KS} = \sum_i [h(i) + V^{KS}(i)]$ and Ψ^{KS} is the total KS wave function, constructed from the first N KS orbitals $\Psi^{KS} = |\phi_1^{KS}\phi_2^{KS} \cdots \phi_N^{KS}|$. If we start from this KS equation instead of Eq. (14) and proceed along the same lines, we derive an expression for the effective potential,

$$V_{eff}(x_1) = V^{KS}(x_1) + V_{kin}^{KS}(x_1) + V^{KS,N-1}(x_1) \ , \tag{37}$$

and, making use of Eq. (32), we reach an expression for V^{KS},

$$V^{KS} = V_{cond} + (V_{kin} - V_{kin}^{KS}) + (V^{N-1} - V^{KS,N-1}) \ . \tag{38}$$

It is reasonable to assume that the differences $(V_{kin} - V_{kin}^{KS})$ and $(V^{N-1} - V^{KS,N-1})$ will be small. It will be shown in Sec. III, however, that the difference between V^{KS} and V_{cond} is not negligible in general.

In the case of a two-electron system the orbital $f(x_1)$ is the same as the Kohn-Sham orbital and $V_{eff} = V^{KS}$ (the potentials V_{kin}^{KS} and $V^{KS,N-1}$ are zero in this case). We can then calculate the Kohn-Sham correlation potential $V_{corr}^{KS}(x_1)$ directly from the effective potential $V_{eff}(x_1)$. The total effective Kohn-Sham potential in DF theory is usually written as a sum of the Coulomb, the exchange, and the correlation potential:

$$V^{KS}(x_1) = \int \frac{\rho(x_2)}{r_{12}} dx_2 + V_x(x_1) + V_{corr}^{KS}(x_1) \ . \tag{39}$$

In a two-electron system only one orbital is doubly occupied, the exchange potential is just the self-interaction correction, and the Hartree-Fock potential is local (and equal to the negative of the exchange potential):

$$V_x(x_1) = -\frac{1}{2} \int \frac{\rho(x_2)}{r_{12}} dx_2 = -V^{HF}(x_1) \ . \tag{40}$$

Because now the total KS potential is the same as the effective potential, we can write down an expression for the correlation potential,

$$V_{corr}^{KS}(x_1) = V_{eff}(x_1) - V^{HF}(x_1)$$

$$= [V_{cond}(x_1) - V^{HF}(x_1)]$$

$$+ V_{kin}(x_1) + V^{N-1}(x_1) \ . \tag{41}$$

There is a slight ambiguity in the definition of the correlation potential as it has not been specified whether V^{HF} is to be evaluated with the HF or with the exact one-electron density. We will always use $V^{HF}[\rho^{exact}]$. The first term in V_{corr}^{KS} may of course be split into a HF contribution and a correction term ($V_{cond} - V^{HF}[\rho^{HF}]$) $- V^{HF}[\Delta\rho]$, where $\Delta\rho = \rho^{exact} - \rho^{HF}$, but it will be observed in Sec. III that the correction term is always small with respect to the difference between conditional and HF potentials. In cases where HF is a good starting point $\Delta\rho$ is small, and in cases where there are strong near-degeneracy effects $\Delta\rho$ becomes large, but so does $V_{cond} - V^{HF}$. In Sec. III we will report on and discuss calculations of the various potentials for the helium atom and the H_2 molecule.

III. RESULTS

Accurate full configuration-interaction (CI) ground-state wave functions were calculated for the hydrogen molecule at the following internuclear distances (a.u.): $0.0(=He),1.0,1.401(=R_e)$, $2.0,3.0,5.0$. For the helium atom a $5s,4p,3d$ Slater-type-orbital basis[24] was used. The Slater functions were expanded in 6 G. For the H_2 molecule, we used a basis consisting of five s-type and two p-type contracted Gaussian-type functions on each nucleus.[25] An extra d-type Gaussian, with $\alpha = 1.0$, was added on both nuclei. In Table I the full CI energies are listed as well as the (almost) exact ground-state energies. The difference is never more than 0.002 hartree and more than 95% of the correlation energy is recovered by the calculated CI functions for all distances.

Also listed in Table I are the ionization energies $E_0^{N-1} - E_0^N$. The energies of the He$^+$ and H_2^+ ions were calculated in the same basis that was used for the calculations on He and H_2. From the full CI wave functions the one-particle density matrix $\gamma(x_1',x_1)$ and the two-particle density matrix $\Gamma^2(x_1',x_2',x_1,x_2)$ were calculated, using a program developed at our laboratory, and these density matrices were used for the calculation of the various po-

TABLE I. Total energies and ionization energies (IE) (in hartree atomic units) for the ground state of the hydrogen molecule at various internuclear distances. E^{corr} refers to the difference $E^{CI}-E^{HF}$. The "exact" values are from Ref. 26 (He, $R=0.0$) and Ref. 27 (all other distances).

R (a.u.)	E^{HF}	E^{CI}	E^{exact}	E^{corr}	IE
0.0 (He)	-2.861	-2.902	-2.904	-0.041	0.902
1.0	-1.085	-1.122	-1.124	-0.037	0.671
1.401	-1.133	-1.172	-1.174	-0.039	0.603
2.0	-1.092	-1.136	-1.138	-0.044	0.534
3.0	-0.989	-1.056	-1.057	-0.067	0.479
5.0	-0.859	-1.0035	-1.0038	-0.1445	0.480

tentials.

Concerning the accuracy of the calculated potentials we want to point out that the only approximation that is made in the procedure is the use of a truncated basis. The best possible (full CI) wave function was calculated in this basis and no further approximations were made in the calculation of the density matrices and the various potentials.

Note that for the calculation of $V_{kin}(x_1)$, Eq. (29), we can avoid taking the second derivative (which can be expected to lead to inaccurate results, especially when Gaussian basis functions are used) if we write this potential, making use of Eq. (21), as

$$V_{kin}(x_1)=[\nabla_{1'}\cdot\nabla_1\gamma(x'_1,x_1)|_{1'=1}]/2\rho(x_1)$$
$$-[\nabla\rho(x_1)]^2/8\rho^2(x_1) . \qquad (42)$$

Now $V_{kin}(x_1)$ is dependent on the first derivative of the basis functions only. At a nucleus the first derivative of a $1s$ Gaussian orbital, centered at that nucleus, is zero. This leads to a wrong behavior of the density near a nucleus so that in this region the two terms on the RHS of (42) may still be inaccurate, e.g., in the He atom these terms both vanish at the nucleus, which is incorrect. However, as demonstrated in Sec. II $V_{kin}(x_1)=0$ at a nucleus. So although both terms in (42) individually behave wrongly in the vicinity of a nucleus, when calculated in a GTF basis, a cancellation of errors occurs and the calculated potential $V_{kin}(x_1)$ correctly goes to zero.

In Figs. 1(a)–4(a) the calculated potentials are displayed for the He atom and for the H_2 molecule at some values of the internuclear distance R. The potentials were calculated and plotted along the bonding axis (z axis). The origin of the plots is the midpoint of the hydrogen molecule [or the He nucleus in Fig. 1(a)]. For the H_2 equilibrium distance $R=1.401$ bohr we also calculated the potentials along two axes perpendicular to the bonding axis, going through the midpoint of the molecule and through one of the nuclei, respectively (Figs. 5 and 6).

For comparison we plotted the sum of the Coulomb and exchange potential

$$V_{Coulomb}(x_1)+V_x(x_1)=\tfrac{1}{2}\int[\rho(x_2)/r_{12}]dx_2 .$$

This potential can be regarded as an exact analog of the Hartree-Fock potential because it is calculated from an exact density. On the scale of the plots shown the true
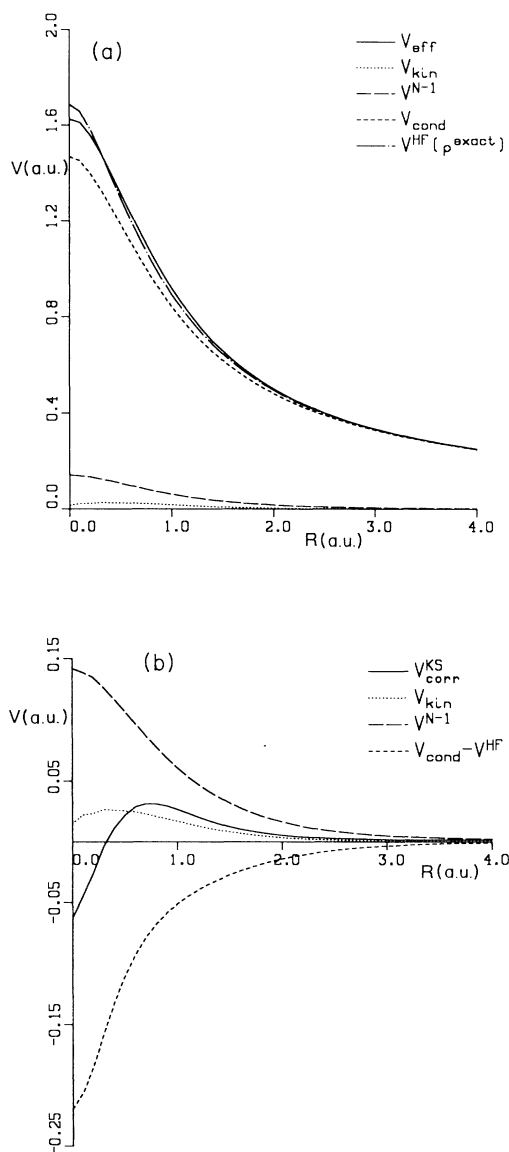

FIG. 1. (a) Potential values for the He atom as a function from the distance from the He nucleus. (b) Kohn-Sham correlation potential for the He atom as a function from the distance from the He nucleus. Also shown are the three contributions that sum to the KS correlation potential, Eq. (41).

HF potential, which is $\frac{1}{2}\int\rho^{HF}(x_2)/r_{12}dx_2$, would be almost indistinguishable from this exact independent-particle potential, except for the distance $R=5.0$, and for this case the HF potential is displayed explicitly [Fig. 4(a)]. In Figs. 1(b)–4(b) the Kohn-Sham correlation potential is displayed as well as the three components that build it [Eq. (41)].

In Table II we list the various orbital expectation values from Eq. (33) that sum to the negative of the ionization potential ε. For completeness, the Hartree-Fock values are also listed. The marginal amplitude f is, in

this case, simply the $1s$ and σ_g orbitals, respectively, while the expectation values of the potentials V_{kin} and V^{N-1} are zero, due to the two-electron character of the He and H_2 systems.

IV. DISCUSSION

A. He

For the helium atom, the Hartree-Fock approximation does extremely well, as far as the density ρ is concerned. The kinetic energy and nuclear attraction energy expecta-
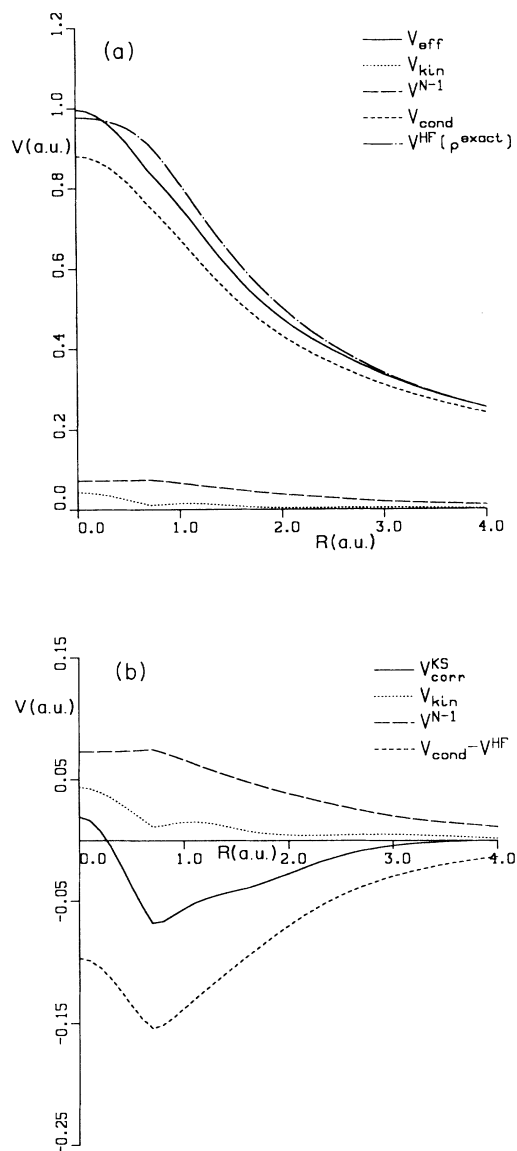

FIG. 2. (a) Potentials for H_2, $R_{H-H}=1.401$ bohr. Potential values along the bond axis. The origin is at the midpoint of the molecule. (b) Kohn-Sham correlation potential and contributions [Eq. (41)] for H_2, $R_{H-H}=1.401$ bohr. Potential values along the bond axis. Origin is at midpoint of molecule.
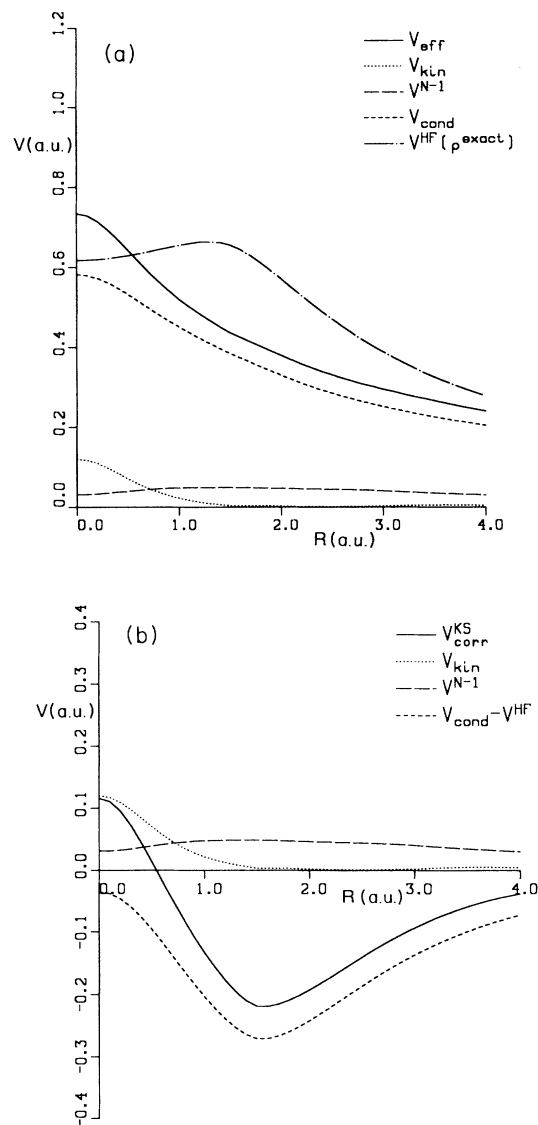
FIG. 3. (a) Potentials for H_2, $R_{H-H}=3.0$ bohr. Potential values along bond axis. Origin is at midpoint of molecule. (b) Kohn-Sham correlation potential and contributions [Eq. (41)] for H_2, $R_{H-H}=3.0$ bohr. Potential values along bond axis. Origin is at midpoint of molecule.

tion values of the (exact) orbital f are almost equal to the HF values for the $1s$ orbital (Table II). This is also illustrated in Fig. 1(a) where we can see that the effective potential and the HF potential are very similar.

In a two-electron system $G^{HF}(x'_1, x_1) = 1$, regardless of the values of r'_1 and r_1, if the spins are equal, $s'_1 = s_1$ and zero when $s'_1 \neq s_1$. This agrees with the well-known fact that in a two-electron Hartree-Fock atom or molecule the exchange hole $-\rho(x_2)|G^{HF}(x_1, x_2)|^2$ is identical to the electron density of the same spin and independent of the position of the reference electron. It follows that $V_{kin}^{HF}(x_1) = 0$. So in a way, we can use V_{kin} as a measure of the independent-particle character of an electron. As

FIG. 5. Potentials for H_2, $R_{H-H} = 1.401$ a.u. Potential values along axis perpendicular to bond axis and going through middle of bond.

we have already noted, V_{kin} is always zero at the nucleus and also in the limit $x_1 \to \infty$ [Fig. 1(a)], and in these regions the electron moves as an independent particle. At about 0.4 a.u. a maximum is reached in V_{kin}, and this is the region where the movement of the electron is correlated most with the other electron in the system. This maximum in V_{kin} still does not differ much from zero, reflecting the fact that in this system, the off-diagonal correlation corrections in the density matrix are small. For the energy, however, these off-diagonal corrections are not unimportant. They lead to a change in kinetic en-
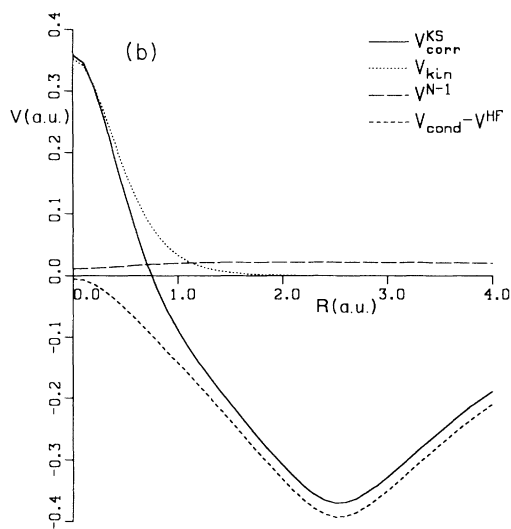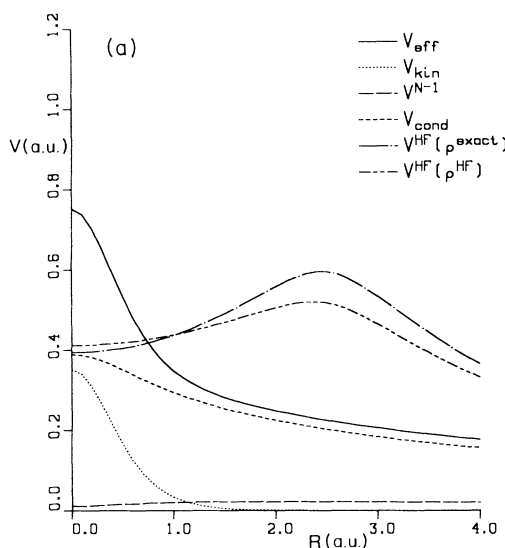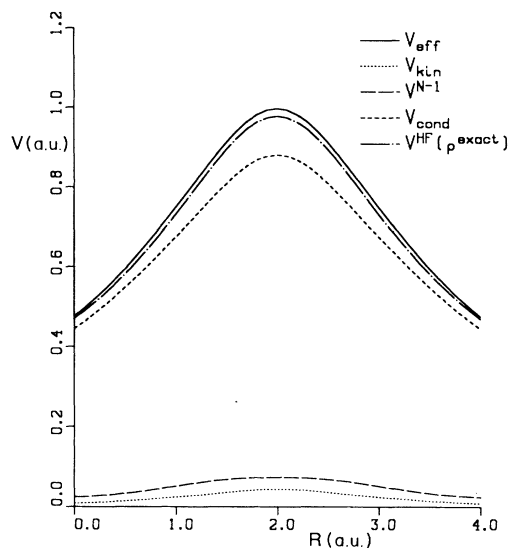

FIG. 4. (a) Potentials for H_2, $R_{H-H} = 5.0$ bohr. Potential values along bond axis. Origin is at midpoint of molecule. (b) Kohn-Sham correlation potential and contributions [Eq. (41)] for H_2, $R_{H-H} = 5.0$ bohr. Potential values along bond axis. Origin is at midpoint of molecule.
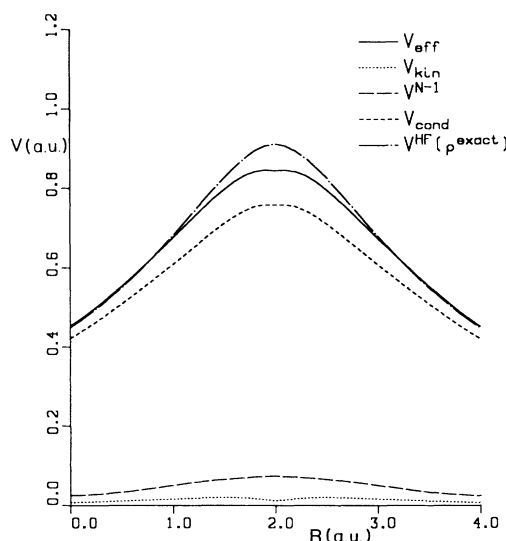

FIG. 6. Potentials for H_2, $R_{H-H} = 1.401$ a.u. Potential values along axis perpendicular to bond axis and going through one of the nuclei.

TABLE II. Expectation values of kinetic and potential-energy operators, Eq. (33), for He $(R = 0.0)$ and H_2, in the exact and HF case. Energy values are in hartree atomic units.

R (a.u.)	$\langle f\|-\frac{1}{2}\nabla^2\|f\rangle$	$\langle f\|V_N\|f\rangle$	$\langle f\|V_{\text{cond}}\|f\rangle$	$\langle f\|V_{\text{kin}}\|f\rangle$	$\langle f\|V^{N-1}\|f\rangle$	ε
0.0 (He)	1.433	-3.376	0.947	0.018	0.076	-0.902
1.0	0.706	-2.121	0.676	0.016	0.052	-0.671
1.401	0.570	-1.824	0.589	0.016	0.046	-0.603
2.0	0.463	-1.542	0.488	0.017	0.040	-0.534
3.0	0.415	-1.310	0.359	0.021	0.036	-0.479
5.0	0.478	-1.192	0.203	0.011	0.020	-0.480
			Hartree-Fock $(f = \sigma_g)$			
0.0 (He)	1.431	-3.373	1.025			-0.918
1.0	0.703	-2.117	0.744			-0.671
1.401	0.563	-1.815	0.658			-0.595
2.0	0.444	-1.521	0.564			-0.514
3.0	0.356	-1.249	0.463			-0.430
5.0	0.325	-1.036	0.364			-0.348

ergy, given approximately by $2\langle f|V_{\text{kin}}|f\rangle = 0.036$ a.u. (Table II) since $\langle f|-\frac{1}{2}\nabla^2|f\rangle$ is almost the same for the HF and exact calculation. This is about equal to the total correlation energy, as it should be since the virial theorem holds for both the Hartree-Fock and the exact wave function.

In a many-electron system $V_{\text{kin}}^{\text{HF}}(x_1)$ is not zero everywhere. The Hartree-Fock kinetic energy $\sum_i n_i \langle \phi_i|-\frac{1}{2}\nabla^2|\phi_i\rangle$ will be different from $N\langle f^{\text{HF}}|-\frac{1}{2}\nabla^2|f^{\text{HF}}\rangle$. The difference is $N\langle f^{\text{HF}}|V_{\text{kin}}^{\text{HF}}|f^{\text{HF}}\rangle$ [see Eq. (25)]. If the system is such that Hartree-Fock is a good approximation, $f^{\text{HF}} \approx f^{\text{exact}}$ and $N\langle f^{\text{HF}}|-\frac{1}{2}\nabla^2|f^{\text{HF}}\rangle \approx N\langle f^{\text{exact}}|-\frac{1}{2}\nabla^2|f^{\text{exact}}\rangle$, as indeed shown in Table II for He. When we go to the exact wave function the difference between $N\langle f^{\text{exact}}|V_{\text{kin}}^{\text{exact}}|f^{\text{exact}}\rangle$ and $N\langle f^{\text{HF}}|V_{\text{kin}}^{\text{HF}}|f^{\text{HF}}\rangle$ will then be approximately equal to the total change in kinetic energy due to correlation, which again, by the virial theorem, will be approximately equal to the total correlation energy. Sierraalta and Ludena analyzed $V_{\text{kin}}(x_1)$ for a few HF atoms.[16] For the neon atom they also calculated $V_{\text{kin}}(x_1)$ from a highly correlated CI function and compared it with the HF result. The two potentials looked very much the same, which led these authors to the conclusion that the function $G(x_1', x_1)$ was essentially only the correlation function for exchange interactions. However, the arguments presented here and in Sec. II and also the calculations on helium show that this conclusion cannot mean that changes in G caused by Coulomb correlation are negligible, at least not as far as the correlation energy is concerned.

The potential $V^{N-1}(x_1)$ is the difference between the energy of the conditional amplitude Φ with reference electron at x_1 and the ground-state energy of the $N-1$ electron system. In Fig. 1(a) we see that this difference is largest at the nucleus and becomes smaller if the reference electron is further out. In the limit $x_1 \to \infty$ the difference is zero; this is an "experimental" example of the asymptotic collapse of the conditional amplitude Φ to

the ground state of the $N-1$ electron system, as was proven by Katriel and Davidson.[13]

It is clear from Fig. 1(a) that the HF potential does not very well represent the average electron repulsion, given by the potential $V_{\text{cond}}(x_1)$. Only if we add the two potentials V_{kin} and V^{N-1} does the difference between the effective and HF potential become small. This difference, which is equal to the Kohn-Sham correlation potential (if we use the exact density for the calculation of the HF potential), is magnified in Fig. 1(b). It resembles very closely the correlation potential calculated by Smith, Jagannathan, and Handler,[10] who calculated the potential directly from a very accurate density, making use of Eq. (1). We note that none of the three terms $V_{\text{cond}} - V^{\text{HF}}$, V_{kin} and V^{N-1} is negligible for the total $V_{\text{corr}}^{\text{KS}}$, which is relatively small as the three contributions partly cancel. $V_{\text{cond}} - V^{\text{HF}}$ is negative, as the probability of finding another electron close to the reference electron is smaller in the correlated system. $V_{\text{cond}} - V^{\text{HF}}$ is dominant close to the nucleus and causes the KS potential to reach a minimum at the nucleus. This reflects the fact that correlation allows for a slightly greater probability of finding an electron in the neighborhood of the nucleus.

The plots in Figs. 1(a) and 1(b) demonstrate the relative insignificance of $V_{\text{corr}}^{\text{KS}}$ compared to V_x (which is equal to $-V^{\text{HF}}$). If approximations are made to the exchange potential considerable care has to be taken[28] that errors made in that approximation are not larger than the whole $V_{\text{corr}}^{\text{KS}}$.

B. H_2

The H_2 molecule is a classical example of a system for which the Hartree-Fock approximation breaks down at large internuclear distances. In Table II we see that the total electron repulsion energy, which for a two-electron system is equal to the expectation value $\langle f|V_{\text{cond}}|f\rangle$, is too high in the HF case and the error increases with the internuclear distance. This error is, of course, a conse-

quence of the near-degeneracy correlation error. If an electron is in the neighborhood of one of the hydrogen nuclei then the probability for the second electron to be found at the other nucleus will increase, depending on the internuclear distance. This correlation is absent in the HF model and at larger internuclear distances the HF potential is much too repulsive at the nuclei. Not only is the electron repulsion energy too high, the much too repulsive HF potential also leads to a wrong density. Especially at larger internuclear distances the expectation values of the operators $-\frac{1}{2}\nabla^2$ and V_N over the density orbital f are very different in the exact and HF case.

In Figs. 2(a) to 4(a) the various potentials are displayed. At equilibrium distance ($R = 1.401$ bohr), where the overlap between the two $1s$ hydrogen orbitals is not small, the effective potential resembles the HF potential, although not as much as in the He case. At large distance (cf. 5 bohr) there is no resemblance at all. The maximum in the HF potential shifts from the middle of the bond at small or intermediate distance to the nuclei at larger distance. This is a direct consequence of the Hartree-Fock error: The ionic contributions to the wave function are much too large and there is too much electron repulsion around the nuclei. The Hartree-Fock density becomes too diffuse and at $R = 5$ bohr the exact $E_{Ne}(=2\langle f|V_N|f\rangle)$ differs, according to Table II, -0.312 a.u. (more stable) from the Hartree-Fock value of E_{Ne}. This is to be compared to a total correlation energy of -0.1445 a.u. The lack of electron-electron correlation in the Hartree-Fock approximation does not just lead to a large error in E_{ee} ($+0.161$ a.u. compared to exact) but to even larger errors in the one-electron terms in the energy: $+0.312$ a.u. in E_{Ne} and -0.328 a.u. in E_K.

The considerable difference between the Hartree-Fock and the exact one-electron densities that is obvious from these energy terms, also leads to a difference between $V^{HF}(\rho^{exact})$ and $V^{HF}(\rho^{HF})$. It is clear from Fig. 4(a) that using the more diffuse ρ^{HF} in V^{HF} leads to a lowering of the repulsive maximum at the nucleus compared to $V^{HF}(\rho^{exact})$. This effect, however, does by no means cancel the strong repulsion that is present in V^{HF} anyway due to the large weight of ionic terms in the wave function. Only the exact electron repulsion potential $V_{cond}(x_1)$ correctly exhibits a strong reduction of the repulsion around a nucleus. $V_{cond}(x_1)$ does not have maxima at the nuclei, but it has a maximum in the middle of the bond. This is true not only for small but also for large internuclear distances. This leads to a considerable contraction of the exact electron density around the nuclei compared to ρ^{HF}. As V_{cond} is so much lower than V^{HF} in that region, the exact electron-electron interaction energy $E_{ee}(=\langle f|V_{cond}|f\rangle)$ is still 0.161 a.u. lower than in the Hartree-Fock approximation. We have noted already that the effect of the contraction is (understandably) much more stabilizing for the electron-nuclear term E_{Ne} (-0.312 a.u.).

It is obvious from Fig. 4(b) that contrary to the situation in He and H_2 at equilibrium distance, where Hartree-Fock is a good approximation, $V_{cond} - V^{HF}$ dominates the Kohn-Sham correlation potential for the near-degeneracy situation in H_2 at large distance. (The contri-

bution of V_{kin} at the bond midpoint is relatively unimportant, see below.) It is clear from the foregoing analysis how the use of V_{cond} rather than V^{HF} in the effective one-electron potential leads to the required improvements in the one-electron density and in the various energy terms.

Turning now to the remaining potentials in V_{corr}^{KS} we first note that the kinetic energy correction potential $V_{kin}(x_1)$ is zero in the limit $x_1 \to \infty$ and on the nuclei (it differs slightly from zero at the nuclei since the basis set fails to describe the electron-nuclear cusp exactly). It has rather low maxima at the outer regions of the molecule, in the regions $R/2 \leq |r_1| \leq \infty$, but it reaches a maximum of considerable height in the middle of the bond. This maximum increases with increasing internuclear distance. In the limit of infinite internuclear distance it reaches the constant value 0.5. This result can easily be obtained from Eqs. (21) and (29) if we insert the (exact) density-matrix expression $\gamma(x_1',x_1)=s_1(x_1')s_1(x_1)+s_2(x_1')s_2(x_1)$, where s_1 and s_2 are the hydrogen-atom orbitals on the two nuclei. The kinetic energy density correction, however, given by $\rho(x_1)V_{kin}(x_1)$, will still be small, so this maximum in V_{kin} at larger internuclear distances does not lead to a large contribution to the correlation energy. This is also clear from Table II. The energy expectation value associated with V_{kin} at first slightly increases with increasing bond distance, so that it remains in the order of $30-40\%$ of the total correlation energy, but from $R = 3.0$ a.u. it goes down again, whereas the correlation energy strongly increases, $\langle f|V_{kin}|f\rangle$ will be zero in the limit of infinite internuclear distance.

We note that the shape of V_{kin} is in agreement with our previous finding that the magnitude of V_{kin} is connected to the rate of change of the conditional amplitude. For positions x_1 of the reference electron somewhere around one nucleus the conditional amplitude reduces to the H $1s$ wave function for the second electron around the other nucleus, and $V_{kin}(x_1)\approx0$. Only when the reference position moves from one nucleus to the other, i.e., around the bond midpoint, does the conditional amplitude change and does V_{kin} attain a significant magnitude. This situation is reminiscent of the one in intershell regions in HF atoms (cf. Sec. II).

The potential V^{N-1} has its maximum at the nuclei, as in helium. At large internuclear distances the whole V^{N-1} becomes very flat with low maxima at the nuclei and a very shallow minimum at the bond midpoint. The energy of the conditional amplitude Φ is therefore almost equal to the H_2^+ ground-state energy, independent of the position of the reference electron. The reason is physically clear. The energy of H_2^+ at large R is the energy of a H atom slightly perturbed by a proton at large distance. If the reference electron is close to the bond midpoint or at infinity, it is far removed from both nuclei and the conditional amplitude will "collapse" to a wave function describing the other electron in the field of two protons at large distance, i.e., H_2^+ with large R. If, on the other hand, the reference electron is close to one proton, the conditional amplitude will describe the other electron as being (almost) certainly close to the other proton and the energy will again be close to that of H_2^+. It will actually

be slightly higher as the stabilization from the *VB* configuration with electron 2 around proton 1 (where the reference electron is) is lacking.

In Fig. 2(b) the Kohn-Sham correlation potential for H_2 at equilibrium distance is displayed. As in helium, a negative minimum is reached at the nuclei while a positive maximum exists in the middle of the bond, making this region less attractive for the electrons. In contrast to the He atom, the potential approaches zero from the negative side in the limit $x_1 \to \infty$. At large distance [$R = 5.0$ bohr, Fig. 4(b)] V_{corr}^{KS} is much larger, as expected from the strong correlation effects, but has, for the reasons discussed above, the same overall shape: Attractive close to the nuclei and repulsive in the middle of the bond. It is not possible to conclude from the investigation that any of the contributions to V_{corr}^{KS} can be neglected. Only at large R is there one dominant term $V_{cond} - V^{HF}$ and is V^{N-1} so flat that it will have very little effect on the eigenfunction f. So when the Hartree-Fock approximation is grossly in error, important improvement may result from taking only, or only approximately, the Coulomb correlation embodied in V_{cond} into account. For real quantitative accuracy, however, the contributions from both V_{kin} and V^{N-1} cannot be neglected. Even if their expectation values over the orbital f (see Table II) are small compared to those of $-\frac{1}{2}\nabla^2$, V_N, and V_{cond}, they are not negligible compared to the differences of those expectation values of their Hartree-Fock counterparts, i.e., to the correlation energy.

V. SUMMARY AND CONCLUSIONS

A one-electron Schrödinger equation, which has the square root of the exact many-electron density $\rho(x_1)$ as a solution, can be derived directly from the N-electron Schrödinger equation. The effective potential V_{eff} in this differential equation is local and can be expressed as a wave function expectation value.[4,7] This wave-function potential relationship makes V_{eff} an interesting object to study. It creates the possibility to analyze in detail the origin and the nature of the various potentials that contribute to V_{eff} and enables one to study correlation in terms of exact local potentials. It is shown in Sec. II how we can distinguish clearly three different contributions to V_{eff} and how we can give physically meaningful interpretations to each of these three terms, making use of the concept of the conditional amplitude Φ.[7] The three contributions are (a) $V_{cond}(x_1)$, the potential at x_1 due to the conditional density of the other electrons in the system given one electron is at x_1 (the Hartree potential plus Coulomb and Fermi hole corrections); (b) $V_{kin}(x_1)$, a potential which, when multiplied by $\rho(x_1)$, corrects for the difference between the exact kinetic energy density and that due to (N times) an electron in the orbital $f(x_1) = N^{-1/2}\rho^{1/2}(x_1)$ [Eq. (26)]. This potential has been shown to provide a local measure of the independent-particle character of an electron: It is small when the probability distribution of the other electrons is insensitive to changes in the reference position x_1. (c) $V^{N-1}(x_1)$, a potential that reflects the deviation of the conditional amplitude $\Phi(x_2,\ldots x_N|x_1)$, considered as an

($N - 1$)-particle wave function parametrically dependent on the reference position x_1, from the ground-state wave function of the $N - 1$ particle system.

We calculated and analyzed these potentials for the helium atom and for the hydrogen molecule at various internuclear distances. These systems are also interesting from a DF point of view because, for two-electron systems, the effective potential is equal to the total Kohn-Sham potential; the KS correlation potential V_{corr}^{KS} can then be obtained simply by subtracting the Coulomb and exchange potential and we can again distinguish three physically meaningful contributions to V_{corr}^{KS} [Eq. (41)].

The relative importance of the three potentials that contribute to V_{corr}^{KS} or V_{eff} is different for He and H_2, due to the different nature of correlation effects found in these systems. In H_2 at longer internuclear distance, correlation is mainly of near-degeneracy, or long-range type, resulting in a large correlation error. In these systems the exact density is often poorly described in the HF approximation. As a consequence, the effective potential will deviate much from the HF potential. We have found that in this situation the conditional potential V_{cond} dominates the effective potential (and $V_{cond} - V^{HF}$ dominates V_{corr}^{KS}). The potential V^{N-1} is small and very flat. It may probably be neglected to a good approximation. This is not so obvious for V_{kin}, although it has been observed that V_{kin} is large only in a region (around the bond midpoint) where $\rho(x_1)$ is small. It is, nevertheless, clear that in the search for good model potentials we must, in near-degeneracy situations, primarily focus our attention at potentials that correctly describe the average electron-electron interaction.

In the He atom and also in H_2 at equilibrium distance the situation is different. These are systems for which HF does very well, although this does not make things much easier from a correlation point of view. The correlation is now mainly of dynamical, or short-range, character. The KS correlation potential is small but, as has been shown, now none of the three potentials that contribute to V_{eff} or V_{corr}^{KS} can be neglected. The correlation energy in these systems is a small and subtle quantity and remains so in the Kohn-Sham picture.

APPENDIX: CONDITIONAL AMPLITUDE CUSP CONDITION

In 1967 Bingel[15] derived the cusp conditions for a molecular wave function $\Psi(x_1 \cdots x_N)$. With x_1 in the neighborhood of nucleus α we can expand $\Psi(x_1 \cdots x_N)$ as

$$\Psi(x_1,x_2 \cdots x_N) = \Psi(0,x_2 \cdots x_N)[1 - Z_\alpha r_1 - dr_1 \cos(v_1)]$$
$$+ O(r_1^2) . \tag{A1}$$

Z_α is the nuclear charge, d a constant (not determined by cusp conditions), r_1 the distance from the nucleus, and v_1 the angle between x_1 and the electric field vector E (produced by the other electrons and nuclei in the system).

We can find an expression for the density $\rho(\mathbf{x}_1)$ from (A1),

$$\rho(\mathbf{x}_1) = \rho(0)[1 - 2Z_\alpha r_1 - 2dr_1\cos(v_1)] + O(r_1^2) . \tag{A2}$$

The derivative of Ψ and ρ at the nucleus, in direction v_1, is then given by

$$\frac{\partial\Psi}{\partial r_1}\bigg|_{r_1=0} = \Psi(0,\mathbf{x}_2\cdots\mathbf{x}_N)[-Z_\alpha - d\cos(v_1)] , \tag{A3}$$

$$\frac{\partial\rho}{\partial r_1}\bigg|_{r_1=0} = \rho(0)[-2Z_\alpha - 2d\cos(v_1)] . \tag{A4}$$

The change of the conditional amplitude $\Phi(\mathbf{x}_2\cdots\mathbf{x}_N|\mathbf{x}_1)$ is given, in general by

$$\begin{aligned}
\nabla_1\Phi(\mathbf{x}_2\cdots\mathbf{x}_N|\mathbf{x}_1) &= \nabla_1[\Psi(\mathbf{x}_1\cdots\mathbf{x}_N)/f(\mathbf{x}_1)] \\
&= N^{1/2}\nabla_1[\Psi(\mathbf{x}_1\cdots\mathbf{x}_N)/\rho^{1/2}(\mathbf{x}_1)] \\
&= [N/\rho(\mathbf{x}_1)]^{1/2}\{\nabla_1\Psi(\mathbf{x}_1\cdots\mathbf{x}_N) - [\nabla_1\rho(\mathbf{x}_1)]\Psi(\mathbf{x}_1\cdots\mathbf{x}_N)/2\rho(\mathbf{x}_1)\} .
\end{aligned} \tag{A5}$$

The change of the conditional amplitude Φ with reference electron on nucleus α is given by

$$\begin{aligned}
\frac{\partial\Phi}{\partial r_1}\bigg|_{r_1=0} &= [N/\rho(0)]^{1/2}\left[\frac{\partial\Psi}{\partial r_1}\bigg|_{r_1=0} - \frac{\partial\rho}{\partial r_1}\bigg|_{r_1=0}\Psi(0,\mathbf{x}_2\cdots\mathbf{x}_N)/2\rho(0)\right] \\
&= [N/\rho(0)]^{1/2}\{\Psi(0,\mathbf{x}_2\cdots\mathbf{x}_N)[-Z_\alpha - d\cos(v_1)] - \rho(0)[-2Z_\alpha - 2d\cos(v_1)]\Psi(0,\mathbf{x}_2\cdots\mathbf{x}_N)/2\rho(0)\} = 0 .
\end{aligned} \tag{A6}$$

[1] W. Kohn and L. J. Sham, Phys. Rev. **136**, B864 (1964).

[2] P. Hohenberg and W. Kohn, Phys. Rev. **140**, A1133 (1965).

[3] G. Hunter, Int. J. Quantum. Chem. **29**, 197 (1986).

[4] M. Levy, J. P. Perdew, and V. Sahni, Phys. Rev. A **30**, 2745 (1984).

[5] E. N. Lasssettre, J. Chem. Phys. **83**, 1709 (1985).

[6] N. H. March, Phys. Rev. Lett. A **113**, 66 (1985); J. Comp. Chem. **8**, 375 (1987).

[7] G. Hunter, Int. J. Quantum. Chem. **9**, 237 (1975); **S9**, 311 (1975).

[8] M. Levy and H. Ou-Yang, Phys. Rev. A **38**, 625 (1988).

[9] N. H. March, Phys. Rev. Lett. A **113**, 476 (1986).

[10] D. W. Smith, S. Jagannathan, and G. S. Handler, Int. J. Quantum. Chem. **S13**, 103 (1979).

[11] C.-O. Almbladh and A. C. Pedroza, Phys. Rev. A **29**, 2322 (1984).

[12] G. Hunter and C. C. Tai, Int. J. Quantum. Chem. **S19**, 173 (1986).

[13] J. Katriel and E. R. Davidson, Proc. Natl. Acad. Sci. U.S.A. **77**, 4403 (1980).

[14] J. C. Slater, Phys. Rev. **91**, 528 (1953).

[15] W. A. Bingel, Theor. Chim. Acta. **8**, 54 (1967).

[16] A. Sierraalta and E. V. Ludena, Int. J. Quantum. Chem. **S20**, 277 (1986).

[17] V. W. Maslen, Proc. Phys. Soc. London Sec. A **69**, 734 (1956).

[18] G. Sperber, Int. J. Quantum Chem. **6**, 881 (1972).

[19] W. L. Luken and D. N. Beratan, Theor. Chim. Acta **61**, 265 (1982).

[20] T. Ziegler and V. Tschinke (private communication).

[21] Y. Tal and R. F. W. Bader, Int. J. Quantum Chem. **S12**, 153 (1978).

[22] L. J. Holleboom, J. G. Snijders, E. J. Baerends, and M. A. Buijse, J. Chem. Phys. **89**, 3638 (1988).

[23] L. J. Holleboom, J. G. Snijders, and E. J. Baerends, Int. J. Quantum Chem. **34**, 289 (1988).

[24] J. D. Doll and W. P. Reinhardt, J. Chem. Phys. **57**, 1169 (1972).

[25] G. L. Lie and E. Clementi, J. Chem. Phys. **60**, 1275 (1974).

[26] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

[27] W. Kolos and L. Wolniewicz, J. Chem. Phys. **41**, 3663 (1964).

[28] A. D. Becke, Int. J. Quantum Chem. **23**, 1915 (1983).