Range Separation Combined With the Overhauser Model: Application to the H_2 Molecule Along the Dissociation Curve

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ABSTRACT: The combination of density-functional theory with other approaches to the many-electron problem through the separation of the electron–electron interaction into a short-range and a long-range contribution (range separation) is a successful strategy, which is raising more and more interest in recent years. We focus here on a range-separated method in which only the short-range correlation energy needs to be approximated, and we model it within the "extended Overhauser approach." We consider the paradigmatic case of the H_2 molecule along the dissociation curve, finding encouraging results. By means of very accurate variational wavefunctions, we also study how the effective electron–electron interaction appearing in the Overhauser model should be to yield the exact correlation energy for standard Kohn-Sham density functional theory. © 2009 Wiley Periodicals, Inc. Int J Quantum Chem 109: 1950–1961, 2009

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1. Introduction

Kohn–Sham (KS) density functional theory (DFT) (see, e.g.,[1]) is a successful method for electronic structure calculations, thanks to its unique combination of low computational cost and reasonable accuracy. In the KS formalism, the total energy of a many-electron system in the external potential $\hat{V}_{ne} = \Sigma_i v_{ne}(\mathbf{r})_i$ is rewritten as a functional of the one-electron density $\rho(\mathbf{r})$,

$$E[\rho] = T_s[\rho] + \int d\mathbf{r} v_{ne}(\mathbf{r})\rho(\mathbf{r}) + U[\rho] + E_{xc}[\rho]. \quad (1)$$

In Eq. (1), $T_s[\rho]$ is the kinetic energy of a noninteracting system of fermions (usually called KS sys-

tem) having the same one-electron density ρ of the physical, interacting, system. The Hartree energy $U[\rho]$ is the classical repulsion energy, $U[\rho] = \frac{1}{2}\int d\mathbf{r} \int d\mathbf{r}'\rho(\mathbf{r})\rho(\mathbf{r}')|\mathbf{r} - \mathbf{r}'|^{-1}$, and the exchange–correlation functional $E_{xc}[\rho]$ must be approximated. Minimization of Eq. (1) with respect to the spin-orbitals forming the KS determinant leads to the KS equations. Thus, instead of the physical problem, in KS DFT we solve the hamiltonian of a model system of noninteracting fermions, and we recover the energy of the physical system via an approximate functional.

Despite its success in scientific areas ranging from material science to biology, approximate KS DFT is far from being perfect, and many fundamental issues still need to be addressed. In particular, KS DFT encounters difficulties in handling near-degeneracy correlation effects (rearrangement of electrons within partially filled shells), and in taking into account long-range van der Waals interaction energies (crucial, e.g., for layered materials and biomolecules). In principle, all the shortcomings of KS DFT come from our lack of knowledge of the exchange–correlation functional, and a huge effort is put nowadays in trying to improve the approximations for $E_{xc}[\rho]$ (for recent reviews see, e.g.,[2, 3]).

An alternative strategy to overcome the problems of DFT is range separation: the electron–electron interaction is split into a long-range and a short-range part, and the two are treated at different levels of approximation [4–27]. Prof. Hirao has been a pioneer in this field, investigating the effect of range separation on the exchange energy with remarkable success (see, e.g.,[4, 5, 18]).

The variant of range separation that we consider here [6–17] can be viewed as a way to remove the constraint that the model system be noninteracting: instead of the KS system, one can define a long-range-only-interacting system (whose wavefunction is thus multideterminantal) having the same density of the physical system. The remaining part of the energy is then approximated with a short-range exchange–correlation functional. The resulting long-range-only hamiltonian, being weakly interacting (and without the electron–electron cusp), can be treated at a reasonable computational cost with standard wavefunction methods: in general, the needed configuration space to achieve good accuracy is small, and often second-order perturbation theory suffices. At the same time, this long-range interaction, albeit small, can make the corresponding wavefunction capture near-degeneracy

effects and long-range van der Waals energies. Provided that the energy functionals are correctly redefined, there is no double counting of the energy, and the method is in principle exact, as it is KS DFT.

As mentioned, this range separated multideterminant DFT needs an approximation for the short-range exchange–correlation functional. One can follow the same path as for KS DFT: start with the local-spin-density approximation (LSDA), consistently constructed as the difference between the standard LSD functional and the exchange–correlation energy of an electron gas with long-range-only interaction [28], and then add gradient corrections (GGA), [11, 12, 14, 29] and eventually meta-gradient corrections (mGGA). However, this path, which proved highly successful for KS DFT, may not be the best for a scheme in which long-range correlations are explicitly taken into account by wavefunction methods. Indeed, in most cases there is no improvement when passing from LSDA to GGA [11, 12, 30], with the exception of hydrogen-bonded complexes [31].

In recent years we have extended the "Overhauser model," an approximate method to calculate the short-range part of the pair density in the uniform electron gas, to systems of nonuniform density [32–35], finding that it yields an accurate description of the short-range part of the spherically- and system-averaged pair density (intracule density) of small atoms. In [35], we have combined the Overhauser equations with the KS equations in a self-consistent way, recovering full CI total energies within 1 mH for the He isoelectronic series. In [34], we have shown that, unlike all the available correlation functionals [36], the model works equally well for the high-density limit of the He and the Hooke's atom series. Thus, on one hand, the Overhauser model seems to be a very good candidate to construct short-range correlation energy functionals. On the other hand, we have tested it only on systems dominated by dynamical correlation: in the He atom, the Overhauser model yields essentially the exact KS correlation energy. However, when we move to systems with strong static correlation we expect the Overhauser model to be unable to yield good results. The combination of the Overhauser model with range-separated multideterminant DFT seems then natural: it can be viewed as a way to produce an adapted short-range correlation functional for the range-separated multideterminant DFT, or as a way to add the description of static correlation to the Overhauser model.

In this work we combine the Overhauser model with range-separated multideterminant DFT, applying it to the case of the H_2 molecule along the dissociation curve, thus analyzing also the case of strong static correlation, as the dissociation limit is approached. The article is organized as follows. After briefly reviewing in Sections 2 and 3 the basic equations of range-separated multideterminant DFT and of the extended Overhauser model, we first analyze in Section 4, using very accurate variational wavefunctions [37–39], how the "exact" electron–electron interaction which appears in the Overhauser model (and that it is usually approximated with a physically-motivated interaction) should be as the H_2 molecule is stretched. This analysis shows the difficulty of modeling static correlation within the Overhauser model. Because the model is only able to describe correlation, we combine it with a generalized OEP scheme for multideterminant DFT, which is described in Section 5. The combination of the two methods is then presented in Section 6, with results for the H_2 molecule. The last Section 7 is devoted to conclusions and perspectives.

2. Multideterminant DFT via Range Separation

Hohenberg and Kohn [40] introduced a universal functional of the density $F[\rho]$, which can be written as a constrained minimum search [41],

$$F[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle. \quad (2)$$

In Eq. (2), the expectation of the kinetic energy operator $\hat{T} = -1/2 \sum_i \nabla_i^2$ plus the Coulomb electron–electron repulsion operator $\hat{V}_{ee} = \sum_{i>j} |\mathbf{r}_i - \mathbf{r}_j|^{-1}$ is minimized over all antisymmetric wavefunctions yielding the density ρ. The universality of the functional $F[\rho]$ stems from the fact that $\hat{T}$ and $\hat{V}_{ee}$ are the same for every electronic system of given particle number $N = \int \rho(\mathbf{r}) d\mathbf{r}$. Kohn and Sham [42] introduced another functional, $T_s[\rho]$ of Eq. (1), by replacing $\hat{V}_{ee}$ in Eq. (2) with zero,

$$T_s[\rho] = \min_{\Phi \to \rho} \langle \Phi | \hat{T} | \Phi \rangle, \quad (3)$$

and used $T_s[\rho]$ for approximating an important part of $F[\rho]$. In Eq. (3), and in the rest of this article, Φ denotes a noninteracting wavefunction (thus in the

majority of cases a single Slater determinant). Similarly, we can introduce a functional $F_{\mathrm{LR}}^\mu[\rho]$ for a long-range-only interaction $\hat{W}_{\mathrm{LR}}^\mu$ (here chosen using the error function, with the real parameter μ governing the cutoff of the short-range part),

$$\hat{W}_{\mathrm{LR}}^\mu = \frac{1}{2} \sum_{i \neq j} \frac{\mathrm{erf}(\mu |\mathbf{r}_i - \mathbf{r}_j|)}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (4)$$

by defining

$$F_{\mathrm{LR}}^\mu[\rho] = \min_{\Psi^\mu \to \rho} \langle \Psi^\mu | \hat{T} + \hat{W}_{\mathrm{LR}}^\mu | \Psi^\mu \rangle \quad (5)$$

in this way we have

$$\lim_{\mu \to \infty} F_{\mathrm{LR}}^\mu[\rho] = F[\rho] \quad (6)$$

$$\lim_{\mu \to 0} F_{\mathrm{LR}}^\mu[\rho] = T_s[\rho]. \quad (7)$$

We can then write the total energy of a given many-electron system as

$$E[\rho] = F_{\mathrm{LR}}^\mu[\rho] + \int d\mathbf{r}\, v_{\mathrm{ne}}(\mathbf{r}) \rho(\mathbf{r})$$

$$+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') \frac{\mathrm{erfc}(\mu |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} + E_{\mathrm{xc}}^\mu[\rho], \quad (8)$$

where $\mathrm{erfc}(x) = 1 - \mathrm{erf}(x)$ is the complementary error function. As in KS DFT then, minimization is performed over the wavefunction Ψ^μ,

$$E_0 = \min_{\Psi^\mu} \left\{ \langle \Psi^\mu | \hat{T} + \hat{W}_{\mathrm{LR}}^\mu | \Psi^\mu \rangle + \int d\mathbf{r}\, v_{ne}(\mathbf{r}) \rho_{\Psi^\mu}(\mathbf{r}) \right.$$

$$\left. + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho_{\Psi^\mu}(\mathbf{r}) \rho_{\Psi^\mu}(\mathbf{r}') \frac{\mathrm{erfc}(\mu |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} + E_{\mathrm{xc}}^\mu[\rho_{\Psi^\mu}] \right\}, \quad (9)$$

where ρ_{Ψ^μ} is the density corresponding to Ψ^μ. Equation (9) yields an effective, long-range-only-interacting hamiltonian to be solved with a chosen wavefunction method. The short-range exchange–correlation functional $E_{\mathrm{xc}}^\mu[\rho]$ is then defined as the energy needed to make Eq. (8) exact,

$$E_{xc}^{\mu}[\rho] = F[\rho] - F_{LR}^{\mu}[\rho]$$
$$- \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r})\rho(\mathbf{r}') \frac{\text{erfc}(\mu|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|}. \quad (10)$$

For instance, the correct LSD approximation to $E_{xc}^{\mu}[\rho]$ is

$$E_{xc}^{\mu,\text{LSD}}[\rho] = \int \rho(\mathbf{r})\{\epsilon_{xc}(\rho_\uparrow(\mathbf{r}),\rho_\downarrow(\mathbf{r})) - \epsilon_{xc}^{\mu}(\rho_\uparrow(\mathbf{r}),\rho_\downarrow(\mathbf{r}))\},$$
$$(11)$$

where $\epsilon_{xc}(\rho_\uparrow(\mathbf{r}),\rho_\downarrow(\mathbf{r}))$ is the exchange–correlation energy per electron of the standard uniform electron gas (with Coulomb electron–electron interaction) and $\epsilon_{xc}^{\mu}(\rho_\uparrow(\mathbf{r}),\rho_\downarrow(\mathbf{r}))$ is the exchange–correlation energy per electron of a uniform electron gas with interaction erf $(\mu r_{12})/r_{12}$ [28].

An exact expression for $E_{xc}^{\mu}[\rho]$ is found from the adiabatic connection formula [16, 43]:

$$E_{xc}^{\mu}[\rho] = \int_{\mu}^{\infty} d\mu' \int_0^{\infty} 4\pi r_{12}^2 f^{\mu'}(r_{12}) \frac{2}{\sqrt{\pi}} e^{-\mu'^2 r_{12}^2} dr_{12}$$
$$- \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r})\rho(\mathbf{r}') \frac{\text{erfc}(\mu|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \quad (12)$$

where $f^{\mu}(r_{12})$ is the spherically and system-averaged pair density (intracule density) obtained by integrating $|\Psi^{\mu}|^2$ over all variables but $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$,

$$f^{\mu}(r_{12}) = \frac{N(N - 1)}{2}$$
$$\times \sum_{\sigma_1 \ldots \sigma_N} \int |\Psi^{\mu}(\mathbf{r}_{12},\mathbf{R},\mathbf{r}_3, \ldots ,\mathbf{r}_N)|^2 \frac{d\Omega_{r12}}{4\pi}$$
$$\times d\mathbf{R} d\mathbf{r}_3 \ldots d\mathbf{r}_N, \quad (13)$$

with $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$. The gaussian damping appearing in Eq. (12) comes from the derivative of the long-range interaction erf$(\mu r_{12})/r_{12}$ with respect to μ, and shows that the exchange–correlation energy is determined by the short-range part of the intracule density. Notice that when $\mu = 0$, Eq. (12) yields the KS exchange–correlation energy functional from a nonlinear adiabatic connection [16, 43].

3. The Extended Overhauser Model

The extended Overhuaser model consists in writing an effective Schrödinger-like equation for the intracule density $f(r_{12})$ of a given system. The basic idea is the following [32, 33, 35]. We start with the observation that the intracule density $f(r_{12})$ couples to any electron–electron interaction operator depending only on the interelectronic distance, $\hat{W} = \Sigma_{i>j} w(|\mathbf{r}_i - \mathbf{r}_j|)$, in the same way as the density $\rho(\mathbf{r})$ couples to any local one-body potential operator $\hat{V} = \Sigma_i v(\mathbf{r}_i)$, i.e.,

$$\langle\Psi|\hat{W}|\Psi\rangle = \int d\mathbf{r}_{12} f(r_{12})w(r_{12}), \quad (14)$$

$$\langle\Psi|\hat{V}|\Psi\rangle = \int d\mathbf{r}\rho(\mathbf{r})v(\mathbf{r}). \quad (15)$$

We can then follow the Hohenberg and Kohn philosophy but with the roles of $\rho(\mathbf{r})$ and $f(r_{12})$, and of $\hat{V}_{ne}$ and $\hat{V}_{ee}$, interchanged. That is, in analogy with Eq. (2) we can define a system-dependent functional $G[f]$,

$$G[f] = \min_{\Psi\to f} \langle\Psi|\hat{T} + \hat{V}_{ne}|\Psi\rangle, \quad (16)$$

so that the total energy of a given physical system is equal to

$$E[f] = G[f] + \int d\mathbf{r}_{12} \frac{f(r_{12})}{r_{12}}. \quad (17)$$

Like KS, we can define another functional by setting $\hat{V}_{ne}$ equal to zero in Eq. (16),

$$T_f[f] = \min_{\Psi\to f}\langle\Psi|\hat{T}|\Psi\rangle. \quad (18)$$

The functional $T_f[f]$ corresponds to the internal kinetic energy of a free (zero external potential) cluster of fermions having the same intracule density of the physical system. The fermions of this cluster interact with an effective interaction $w_{eff}(r_{12})$ which has the same role of the KS potential for the KS system. In practice, this effective interaction must be approximated. Moreover, for $N > 2$ electrons the cluster equation becomes a complicated many-body problem, so that other approximations

are needed. As in the original Overhauser model for the uniform electron gas [44, 45], we can approximate the cluster equation with a set of radial geminals $g_i(r_{12})$,

$$\left[-\frac{1}{r_{12}}\frac{d^2}{dr_{12}^2}r_{12} + \frac{\ell(\ell+1)}{r_{12}^2} + w_{\text{eff}}(r_{12}) \right] g_i(r_{12}) = \epsilon_i g_i(r_{12}),$$

$$\sum_i \vartheta_i |g_i(r_{12})|^2 = f(r_{12}), \quad (19)$$

whose occupancies ϑ_i must be defined (e.g., in a determinantal-like way as in the original Overhauser model [45]). In practice, trying to solve the whole many-electron Schrödinger equation by means of Eqs. (17)–(19) is a daunting task. The idea is rather [32, 33, 35] to couple this "average-pair-density-functional theory" with a density functional scheme: Eqs. (19) can be generalized to any $f^\mu(r_{12})$ along the adiabatic connection of DFT. In [32, 35], we started from the effective interaction $w_{\text{eff}}^{\text{KS}}(r_{12})$ that, when inserted in Eqs. (19), gives the intracule density corresponding to the KS system, $f_{\text{KS}}(r_{12})$ (that can be obtained from the KS determinant). We then wrote an approximation for $w_{\text{eff}}^\mu(r_{12})$ along the long-range adiabatic connection of DFT as

$$w_{\text{eff}}^\mu(r_{12}) = w_{\text{eff}}^{\text{KS}}(r_{12}) + w_{\text{eff}}^{c,\mu}(r_{12}). \quad (20)$$

The only term that needs to be approximated is then $w_{\text{eff}}^{c,\mu}(r_{12})$, an effective interaction that should essentially "tell" to the intracule density that, while the electron–electron interaction is turned on (i.e. as μ increases), the one-electron density $\rho(\mathbf{r})$ does not change. As the information on $\rho(\mathbf{r})$ has been "washed away" in the integration over the center of mass $\mathbf{R}$ of Eq. (13), this constraint can be imposed only in an approximate way. For two-electron atoms, for which Eq. (19) is exact with one geminal [33], $g = \sqrt{f}$, a simple approximation for $w_{\text{eff}}^{c,\mu}(r_{12})$ is [32, 34, 35]

$$w_{\text{eff}}^{c,\mu}(r_{12}) = \frac{\text{erf}(\mu r_{12})}{r_{12}} - \left(\frac{4\pi}{3}\bar{r}_s^3\right)^{-1} \int_{|\mathbf{x}|\leq\bar{r}_s} \frac{\text{erf}(\mu|\mathbf{r}_{12}-\mathbf{x}|)}{|\mathbf{r}_{12}-\mathbf{x}|} d\mathbf{x},$$

$$(21)$$

where $\bar{r}_s$ is a screening length associated to the radius of a sphere containing on average one electron [44–46]. The physical idea behind Eq. (21) is to mimic the constraint of fixed one-electron density by screening the electron–electron interaction over

a length associated to the "space" available to each electron (which is determined by the density). Indeed, for the He isoelectronic series Eqs. (12), (19), and (21), combined self-consistently with the KS equations, recover the full CI total energy within 1 mH [32, 34, 35].

4. The Overhauser Model for the H₂ Molecule: How Things Should Be

For a closed-shell physical electronic system (atom, molecule) with $N = 2$ particles, the Schrödinger equation describing the internal degrees of freedom of a cluster of fermions having the same intracule density $f(r_{12})$ is exactly given by [33–35]

$$\left[-\frac{1}{r_{12}}\frac{d^2}{dr_{12}^2}r_{12} + w_{\text{eff}}(r_{12}) \right] \sqrt{f(r_{12})} = \varepsilon \sqrt{f(r_{12})}. \quad (22)$$

As a first study, we calculate and analyze the "exact" Overhauser interaction $w_{\text{eff}}(r_{12})$ at full coupling strength (i.e., for electron–electron interaction $1/r_{12}$, corresponding to $\mu = \infty$) for the H₂ molecule at different values of the internuclear distance R, and we compare it with the approximation of Eq. (21). To this purpose, we need extremely accurate intracule densities $f(r_{12})$, which are described in the Section 4.1.

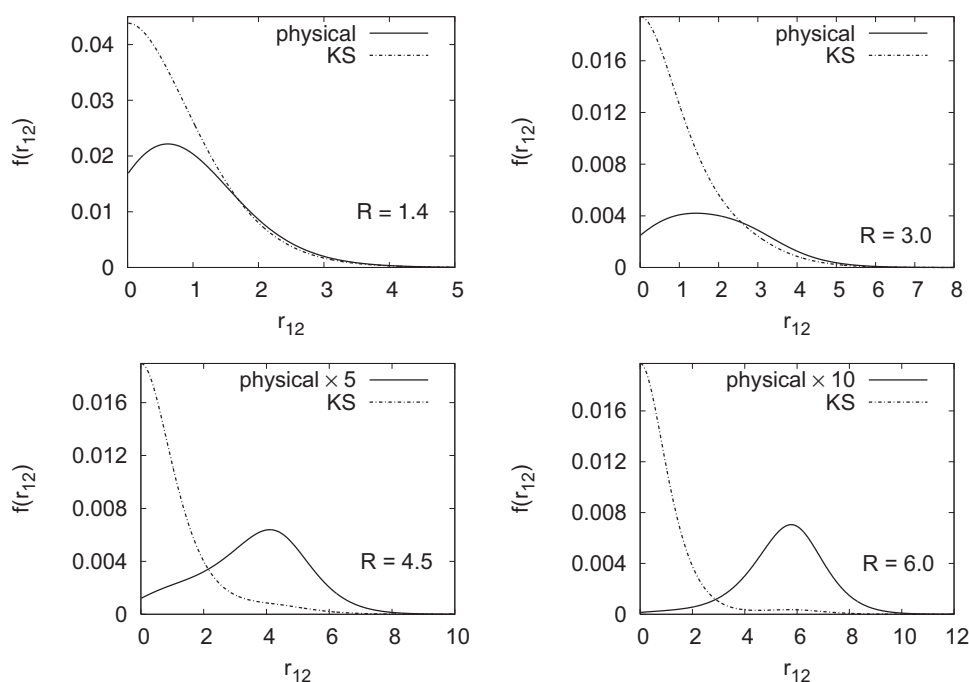### 4.1. INTRACULE DENSITIES FROM ACCURATE VARIATIONAL WAVEFUNCTIONS

We use the accurate variational wavefunctions of [37–39], which are expanded in explicitly correlated gaussian geminals,

$$\Psi(\mathbf{r}_1,\mathbf{r}_2) = (1 + \hat{P}_{12})(1 + \hat{\imath}_e)\sum_{k=1}^{K} c_k \psi_k(\mathbf{r}_1,\mathbf{r}_2) \quad (23)$$

$$\psi_k(\mathbf{r}_1,\mathbf{r}_2) = e^{-\alpha_k|\mathbf{r}_1-\mathbf{r}_{Ak}|2}e^{-\beta_k|\mathbf{r}_2-\mathbf{r}_{Bk}|2}e^{-\gamma_k r_{12}^2}, \quad (24)$$

where $\mathbf{r}_{Ak}$ and $\mathbf{r}_{Bk}$ are centers that lie on the internuclear axis, $\hat{P}_{12}$ means permutation of $\mathbf{r}_1$ and $\mathbf{r}_2$, and $\hat{\imath}_e$ is the inversion operator with respect to the center of the molecule. The parameters appearing in Eqs. (23) and (24) are determined variationally by minimizing the energy with the conjugate gradient method (for more details on the wavefunction and the algorithms employed, see [37–39].). The expansion length $K = 1200$

FIGURE 1. Intracule densities $f(r_{12})$ for the H_2 molecule at different internuclear distances R for the physical system (from the accurate variational wavefunction described in Section 4.1) and for the KS system (from the density corresponding to the same accurate variational wavefunctions).

in Eq. (23) is used, resulting in energies with the extraordinary accuracy of 10^{-10} Hartree.

The intracule densities $f(r_{12})$ from these extremely accurate wavefunctions can be easily calculated, because all the needed integrals are analytic. We also calculated the one electron densities $\rho(\mathbf{r})$, and the intracule densities $f_{KS}(r_{12})$ corresponding to the KS system, which can be obtained by inserting in Eq. (13) the KS wavefunction $1/2\sqrt{\rho(\mathbf{r}_1)}\sqrt{\rho(\mathbf{r}_2)}$. In Figure 1, we show the intracule densities $f(r_{12})$ and $f_{KS}(r_{12})$ for the internuclear distances $R = 1.4$, 3.0, 4.5, and 6.0 a.u. Although mathematically the wave function of Eqs.(23)–(24) is cuspless, we see that the very elaborate ansatz permits to describe the exact linear behavior of the intracule density for $r_{12} \rightarrow 0$, up to extremely short distances. Figure 2 shows the same quantities multiplied by the volume element $4\pi r_{12}^2$. This figure better visualizes the transition from dynamical to static correlation. In Figure 3, we also report the same quantities in the extreme stretched case, $R = 20$, obtained from the simple Heitler–London wavefunction.

4.2. ACCURATE OVERHAUSER POTENTIALS

From the accurate intracule densities of the previous subsection we can calculate, by inversion,

the corresponding "exact" Overhauser interaction $w_{\text{eff}}(r_{12})$,

$$w_{\text{eff}}(r_{12}) = \frac{1}{\sqrt{f(r_{12})}} \frac{1}{r_{12}} \frac{d^2}{dr_{12}^2}(r_{12}\sqrt{f(r_{12})}) + \text{const.} \quad (25)$$

The inversion of Eq. (25) is done numerically, by finite differences. In Figure 4, we report the effective Overhauser interactions that, when inserted in Eq. (22), give the physical and the KS intracule, corresponding, respectively, to $\mu = \infty$ and $\mu = 0$ along the long-range adiabatic connection of Section 2 (or to $\lambda = 1$ and $\lambda = 0$ along the usual linear adiabatic connection in which $\hat{V}_{\text{ee}}$ is simply multiplied by λ). We see that $w_{\text{eff}}(r_{12})$ for large r_{12} goes to the same constant for both the KS and the physical system, as it should be [35] (of course if we go to too large r_{12} we start to observe the wrong harmonic wall due to the gaussian asymptotic decay of our wavefunction). The difference between the effective Overhauser interaction for the physical and the KS system gives $w_{\text{eff}}^{c,\mu \rightarrow \infty} \equiv w_{\text{eff}}^c$ of Eq. (20), and is reported in Figure 5, where also the Coulomb repulsion $1/r_{12}$ is shown. From this figure, we see that, when the system is still dominated by dynamical correlation, as in the case $R = 1.4$ and $R = 3$, $w_{\text{eff}}^c(r_{12})$
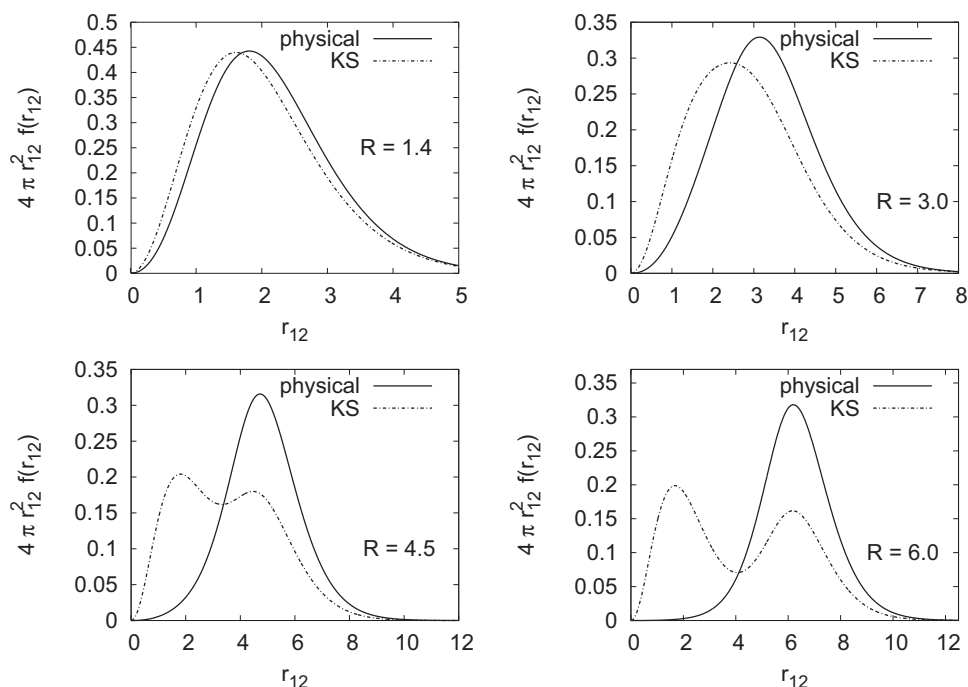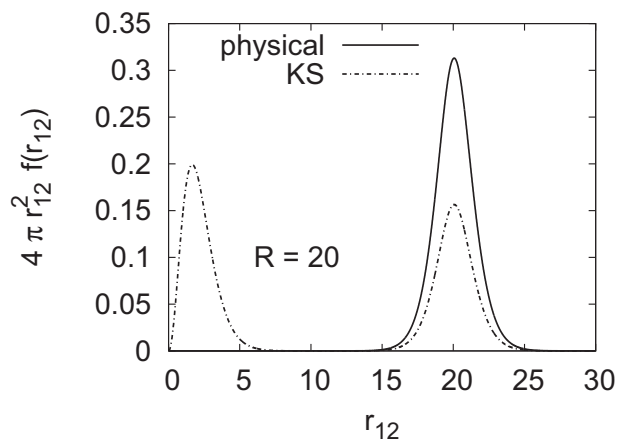
FIGURE 2. The same intracule densities of Figure 1 multiplied by the volume element $4\pi r_{12}^2$.

is essentially a screened Coulomb interaction. That is, for short-range it behaves as $1/r_{12}$, and then for large r_{12} goes to zero much faster than $1/r_{12}$. In such cases, the approximation of Eq. (21), which at $\mu = \infty$ reads

FIGURE 3. The intracule density $f(r_{12})$ multiplied by the volume element $4\pi r_{12}^2$ for the H_2 molecule in the extreme stretched case $R = 20$. The physical $f(r_{12})$ has been calculated from the simple Heitler-London wavefunction, and $f_{KS}(r_{12})$ from its corresponding density.

$$w_{\text{eff}}^c(r_{12}) = \frac{1}{r_{12}} + \frac{r_{12}^2}{2\bar{r}_s^3} - \frac{3}{2r_s} \quad r_{12} \leq \bar{r}_s$$
$$w_{\text{eff}}^c(r_{12}) = 0 \qquad r_{12} > \bar{r}_s \tag{26}$$

can work reasonably well, with a screening length $\bar{r}_s \sim R$. However, as R grows and the system starts to be dominated by static correlation, we see that the approximation of Eq. (26) cannot work: the "exact" $w_{\text{eff}}^c(r_{12})$ still decays much faster than $1/r_{12}$ for large r_{12}, but at short range is more repulsive than the Coulomb interaction! i.e., we need an "overscreened" interaction. This is completely evident in the extreme stretched case $R = 20$ of Figure 6, again obtained from the simple Heitler–London wavefunction.

5. Generalized Optimized Effective Potential Method for Multideterminant DFT

In recent years, the focus of a large part of the scientific community working on improving the approximations for $E_{\text{xc}}[\rho]$ has shifted from seeking explicit functionals of the density (like the generalized gradient approximations), to implicit functionals, typ-
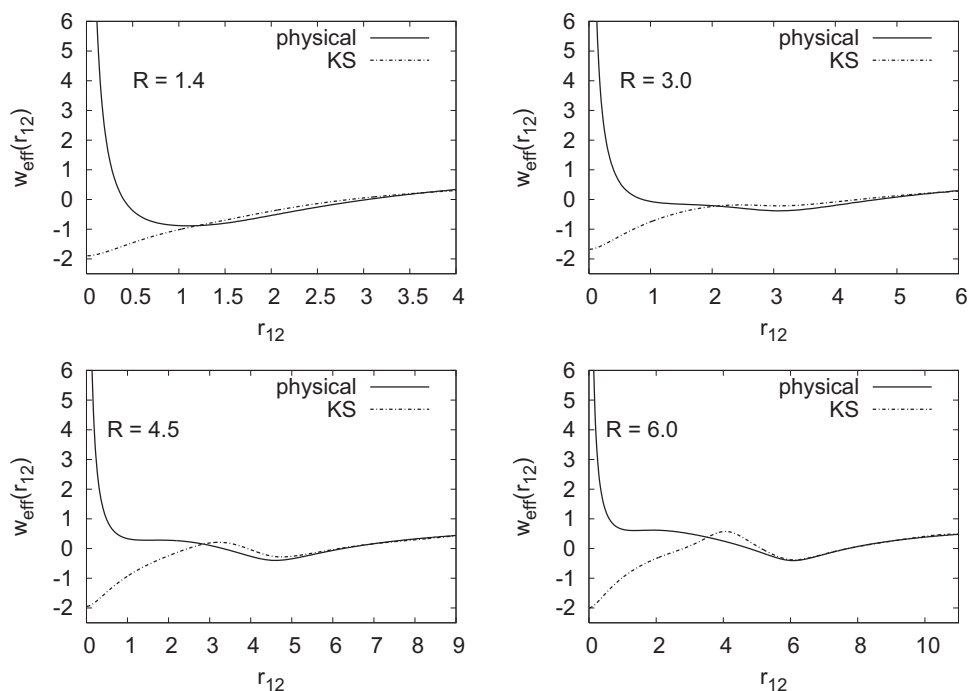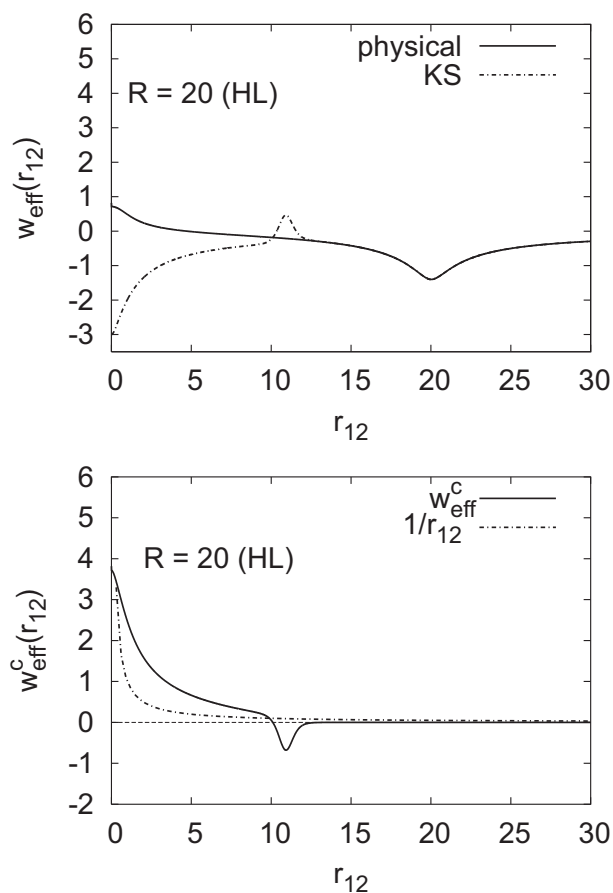
FIGURE 4. The "exact" effective Overhauser interaction $w_{eff}(r_{12})$ for the intracule densities of the physical and of the KS systems of Figure 1.
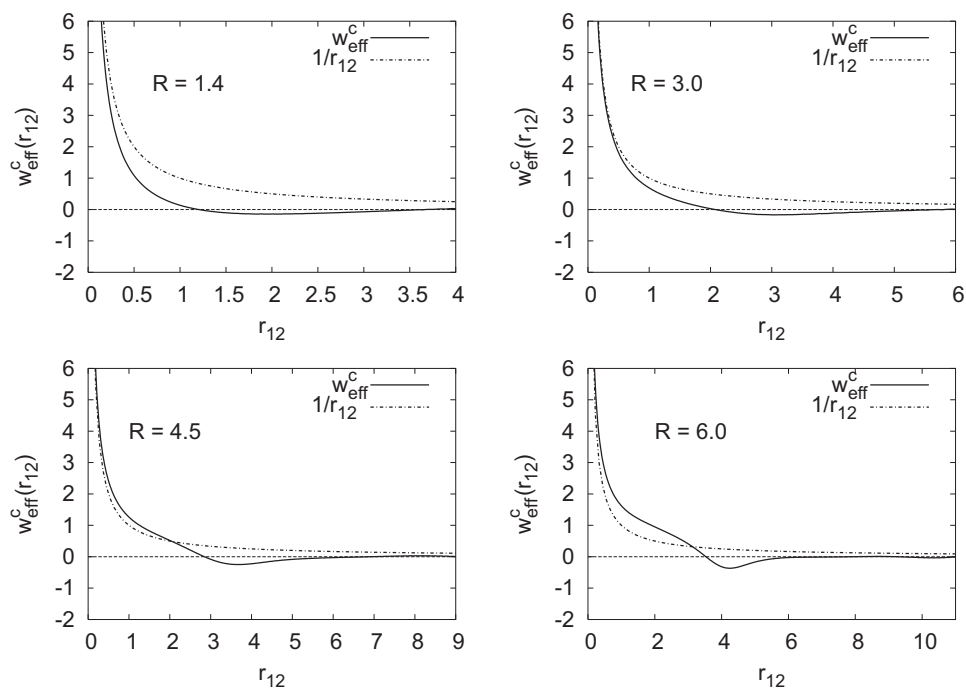
FIGURE 5. The difference $w_{eff}^c(r_{12})$ between the "exact" effective Overhauser interaction for the intracule density of the physical and of the KS systems of Figure 4. The Coulomb repulsion $1/r_{12}$ is also reported.

FIGURE 6. Same as Figures 4 and 5 for the extreme stretched molecule, using the simple Heitler–London wavefunction.

$$E_c^\mu[\rho] = E_{xc}^\mu[\rho] - E_x^\mu[\rho], \qquad (28)$$

but we can also define a multideterminantal (md) exchange functional [10] by using the wavefunction Ψ^μ,

$$E_{x,md}^\mu[\rho] = \langle \Psi^\mu | \hat{V}_{ee} - \hat{W}_{LR}^\mu | \Psi^\mu \rangle$$

$$- \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r})\rho(\mathbf{r}') \frac{\text{erfc}(\mu|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|}, \quad (29)$$

and then a corresponding correlation energy that recovers the energy missed by Ψ^μ (which is smaller than the energy missed by the KS determinant Φ),

$$E_{c,md}^\mu[\rho] = E_{xc}^\mu[\rho] - E_{x,md}^\mu[\rho]. \qquad (30)$$

Then, with this latter definition of the correlation energy, the generalized OEP-like scheme for multi-determinant DFT becomes [10]

$$E_0 = \inf_{v^\mu} \{ \langle \Psi_{v^\mu}^\mu | \hat{T} + \hat{V}_{ee} + \hat{V}_{ne} | \Psi_{v^\mu}^\mu \rangle + E_{c,md}^\mu[\rho_{\Psi_{v^\mu}^\mu}] \},$$

$$(31)$$

where $\Psi_{v^\mu}^\mu$ is obtained by solving the Schrödinger equation corresponding to the hamiltonian

$$\hat{H}^\mu = \hat{T} + \hat{W}_{LR}^\mu + \hat{V}^\mu, \quad \hat{V}^\mu = \sum_i v^\mu(\mathbf{r}_i). \qquad (32)$$

Notice that this multideterminant OEP scheme is different from the one recently proposed in [48]. In Eq. (31), the weak long-range interaction $\hat{W}_{LR}^\mu$ automatically selects the configuration space needed to yield an accurate solution for the hamiltonian $\hat{H}^\mu$ of Eq. (32), whereas in [48], the configuration space is chosen essentially by hand, using physical and chemical intuition. In fact, when the KS system is degenerate or near-degenerate, even a weak interaction (i.e., in our case, a small μ) is able to capture the near-degenerate configurations. At the same time, if we choose a small value of μ, the configuration space needed to yield an accurate description of Ψ^μ is small, and often the few near-degenerate states are enough. This is shown quantitatively, e.g., in Figure 3 of [8], for the case of the Be atom.

In the next Section 4, we use the Overhauser model to approximate $E_{c,md}^\mu[\rho]$, and we apply our combined formalism to the case of the H_2 molecule.

ically using the exact exchange $E_x[\rho]$, which is only explicitly known in terms of the KS orbitals $\phi_i(\mathbf{r})$. The corresponding KS potential must then be computed with the optimized effective potential (OEP) method (for a recent review, see [47]). The OEP scheme can be generalized to the multideterminant range-separated DFT by first noticing that we can divide $E_{xc}^\mu[\rho]$ into exchange and correlation in two different ways [10]: we can define the exchange energy with respect to the KS determinant Φ,

$$E_x^\mu[n] = \langle \Phi | \hat{V}_{ee} - \hat{W}_{LR}^\mu | \Phi \rangle$$

$$- \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \, \rho(\mathbf{r})\rho(\mathbf{r}') \frac{\text{erfc}(\mu|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \qquad (27)$$

and then define the usual correlation energy functional $E_c^\mu[\rho]$ as the energy missed by the KS wavefunction,

6. Multideterminant DFT Combined With the Overhauser Model

From the adiabatic connection formalism we can easily write an exact formula for $E_{c,md}^\mu[\rho]$,

$$E_{c,md}^\mu[\rho] = \int_\mu^\infty d\mu' \int_0^\infty 4\pi r_{12}^2 [f^{\mu'}(r_{12})$$

$$- f^\mu(r_{12})] \frac{2}{\sqrt{\pi}} e^{-\mu'^2 r_{12}^2} dr_{12}, \quad (33)$$

which shows that $E_{c,md}^\mu[\rho]$ is determined by the change in the short-range part of the intracule density when the electron–electron interaction increases from $\mathrm{erf}(\mu r_{12})/r_{12}$ to the full Coulomb repulsion $1/r_{12}$. By adding and subtracting $f_{KS}(r_{12})$, Eq. (33) can also be written as

$$E_{c,md}^\mu[\rho] = E_c^\mu[\rho] - \int_0^\infty 4\pi r_{12}^2 [f^\mu(r_{12})$$

$$- f_{KS}(r_{12})] \frac{\mathrm{erfc}(\mu r_{12})}{r_{12}} dr_{12}, \quad (34)$$

where $E_c^\mu[\rho]$ is the correlation energy of Eq. (28), defined with respect to the KS determinant.

We computed $f^\mu(r_{12})$ within the Overhauser model, Eq. (19) with one geminal $g = \sqrt{f}$, using the simple screened potential of Eqs. (20) and (21) with the screening length $\bar{r}_s = R$. For each internuclear distance R, the intracules $f^\mu(r_{12})$ have been calculated for 33 values of μ between $\mu = 0.01$ and $\mu = 20$. By numerical integration we then computed

$$\frac{\partial E_c^\mu[\rho]}{\partial \mu} = \int_0^\infty 4\pi r_{12}^2 [f^\mu(r_{12}) - f_{KS}(r_{12})] \frac{2}{\sqrt{\pi}} e^{-\mu'^2 r_{12}^2} dr_{12}$$

$$(35)$$

and we fitted the values of $\partial E_c^\mu[\rho]/\partial_\mu$ with the derivative of the function

$$E_c^\mu[\rho] = \frac{a_4}{b^{10}} - \frac{a_1 \mu^6 + a_2 \mu^7 + a_3 \mu^8 + a_4 \mu^{10}}{(1 + b^2 \mu^2)^5}, \quad (36)$$

which has the correct asymptotic behaviors [49]. We also computed, again by numerical integration,

the second term on the right-hand-side of Eq. (34) in order to obtain $E_{c,md}^\mu[\rho]$.

We then implemented the generalized OEP scheme of Eq. (31) by first minimizing the effective potential $v^\mu(\mathbf{r})$ at the "generalized-exchange" -only level, and by adding $E_{c,md}^\mu[\rho]$ only as a final correction. Because $E_{c,md}^\mu[\rho]$ is very small, we do not expect substantial changes by implementing a full self-consistent scheme. Our procedure can be summarized with the equation

$$E_0 = (\inf_{v^\mu} \langle \Psi_{v^\mu}^\mu | \hat{T} + \hat{V}_{ee} + \hat{V}_{ne} | \Psi_{v^\mu}^\mu \rangle) + E_{c,md}^\mu[\rho_{\Psi_{v^\mu}^\mu}], \quad (37)$$

where $E_{c,md}^\mu[\rho_{\Psi_{v^\mu}^\mu}]$ is calculated with the final density resulting from the minimization in the first term on the right-hand-side of Eq. (37).

To carry out the minimization with respect to the potential $v^\mu(\mathbf{r})$ in Eq. (37) we proceeded as follows. We parametrized the potential $v^\mu(\mathbf{r})$ with a simple two-parameter form, by adding to the physical external potential a gaussian centered on each atom, $ce^{-\gamma r^2}$. The minimization of the expectation $\langle \Psi_{v^\mu}^\mu | \hat{T} + \hat{V}_{ee} + \hat{V}_{ne} | \Psi_{v^\mu}^\mu \rangle$ with respect to the two parameters c and γ is done by calculating at each step full-CI wavefunctions $\Psi_{v^\mu}^\mu$ for the hamiltonian with electron–electron interaction $\mathrm{erf}(\mu r_{12})/r_{12}$ and external potential $v^\mu(\mathbf{r})$. All calculations were done at the cc-V5Z basis-set level. We also produced with MOLPRO [50] full CI reference results for the physical hamiltonian, for comparison. Our simple parametrization of the potential v^μ, containing only two parameters, is enough to yield at $\mu = 0$ the HF energy within 0.5 mH, which is the accuracy we sought in this study. This way, we avoid all the well-known problems of the OEP method in finite basis set [51] at the price of obtaining only an upper bound for our minimization problem (yet, with the reasonable accuracy of 0.5 mH).

In Figure 7, we report the results for $E_{c,md}^\mu[\rho]$ for three different values of the internuclear distance R. The dots ($\bullet$) are the "exact" values of $E_{c,md}^\mu[\rho]$, i.e., the full-CI total energies obtained with MOLPRO minus the energies corresponding to the first term on the right-hand-side of Eq. (37), $\inf_{v^\mu} \langle \Psi_{v^\mu}^\mu | \hat{T} + \hat{V}_{ee} + \hat{V}_{ne} | \Psi_{v^\mu}^\mu \rangle$. The solid line is $E_{c,md}^\mu[\rho]$ from the Overhauser model, and the dashed line is the LDA result, obtained from the parametrization of [28], in which $E_{c,md}^\mu[\rho]$ for the uniform electron gas has been calculated with Quantum Monte Carlo methods. We see from this figure that when the system is still dominated by dynamical correlation, as in the $R = 1.4$ and the $R = 2$ cases, the Overhauser model
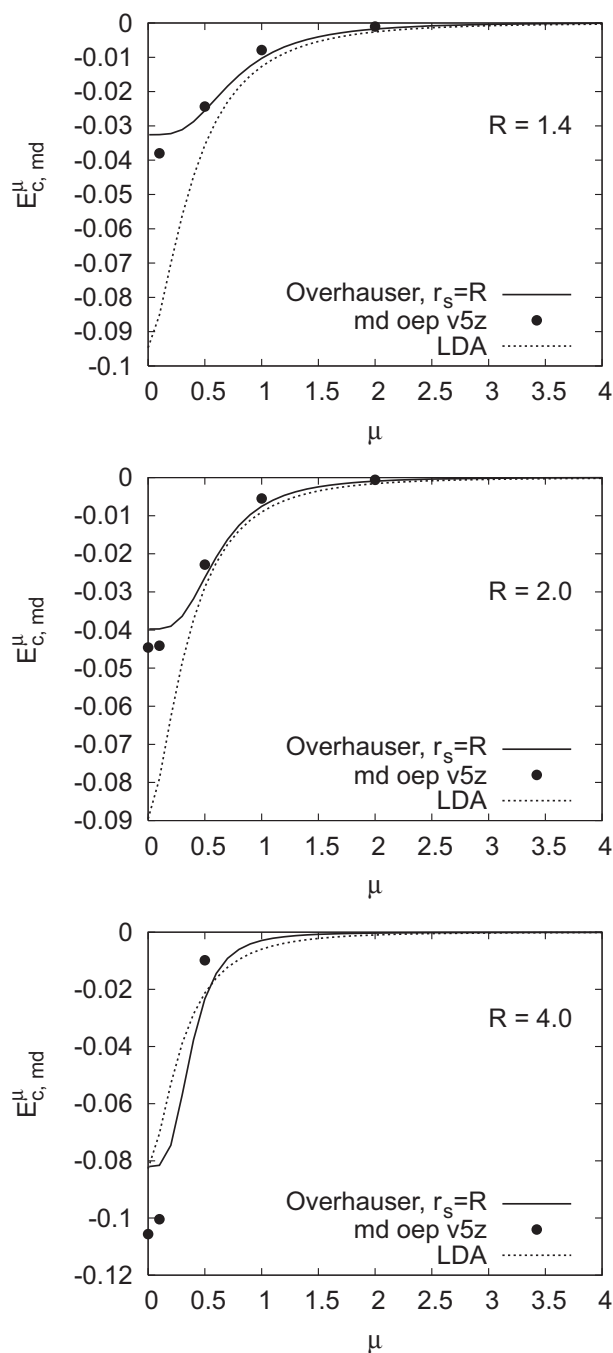
FIGURE 7. The short-range correlation energy for range-separated multideterminant DFT as a function of the cutoff parameter μ for the H_2 molecule at three different values of the internuclear distance R. Dots (●) are "exact" values (see text in Section 6), solid lines are the results from the Overhauser model, and the dashed lines are the LDA values.

yields, even at $\mu = 0$ (i.e. for pure KS DFT), correlation energies with errors of ~ 5 mH (while LDA is off by ~ 60 mH), which reduce to 1 mH at $\mu = 0.5$

(where the LDA error is still ~ 10 mH). We focus here on the value $\mu \sim 0.5$ because it is the one commonly used in practical applications [9–15]. When the system starts to be dominated by static correlation, as in the $R = 4$ case, the Overhauser model with the simple screened potential of Eq. (21) gives, at $\mu = 0$, errors very close to those of LDA (~ 20 mH), which are still of the order of ~ 10 mH at $\mu = 0.5$. As the molecule approaches the dissociation limit, $R \to \infty$, the exact $E_{c,md}^{\mu}[\rho]$ tends to the limiting behavior in which $E_{c,md}^{\mu=0}[\rho] = E_{c}^{KS}[\rho]$, and $E_{c,md}^{\mu}[\rho] = 0$ for any $\mu > 0$. This is due to the fact that, as $R \to \infty$, the long-range only wavefunction Ψ^{μ}, even at very small μ (i.e., with an infinitesimal interaction), becomes essentially exact and equal to the Heitler-London wavefunction, so that the functional should be just equal to zero. In this limit, the Overhauser model is wrong for small μ (because, as explained in Section 4, it misses the "overscreening" at short range), but, for $\mu \gg 0$, yields $E_{c,md}^{\mu}[\rho]$ that go to zero much faster than LDA, as it can be already grasped from the third panel of Figure 7. It is thus still more suitable than LDA to be combined with the range-separated multideterminant DFT, but it definitely needs some improvement.

Notice that the Overhauser model would yield much more accurate results if we were able to compute $E_{c,md}^{\mu}[\rho]$ by using in Eq. (20) instead of $w_{eff}^{KS}(r_{12})$ the interaction $w_{eff}^{\mu}(r_{12})$ which yields the intracule $f^{\mu}(r_{12})$ associated to the wavefunction Ψ^{μ}. This way, we would use the information available in Ψ^{μ} to the maximum extent, and we would not have the problems associated to the "overscreening" discussed in Section 4. This possibility will be investigated in future work.

7. Conclusions and Perspectives

We have presented a preliminary study of the combination of range-separated multideterminant DFT with the Overhauser model, with an application to the paradigmatic case of the H_2 molecule. We have first analyzed, by means of very accurate variational wavefunctions, the failure of the Overhauser model in describing static correlation and we have then used it to produce an adapted short-range correlation functional for range-separated multideterminant DFT. The results are very good for internuclear distances close to equilibrium, and are still encouraging as the molecule is stretched. Indeed, in the dissociation limit the exact short-range correlation functional should go to zero for any $\mu > 0$, and the Overhauser model

yields short-range correlation energies that go to zero faster than LDA as μ increases.

Future work will address the study of better approximations for the unknown Overhauser electron–electron interaction, and the development of a more efficient scheme to combine it with range-separated multideterminant DFT.

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