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Beyond the Kohn-Sham Determinant

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Abstract

Several schemes which extend the Kohn–Sham construction to multideterminantal wavefunctions are possible. The following ones are presented:

- use of the eigenfunctions of $\hat{S}^2$
- selection of a reference orbital space
- splitting of the electron-electron interaction operator

With multideterminantal wavefunctions, it is necessary to replace the dependence of the functionals on the spin-density by that of a dependence on the on-top pair density.

Introduction

The present paper shows some efforts towards extending the approach of Kohn and Sham [1]. The selection of items presented is personal and by no means covers the literature on this subject. None of the methods presented has been widely used. For some of them, however, the existing numerical material is sufficient to draw conclusions about their performance. Other methods are only sketched as there is little or no experience with them. They are presented, as they might give indications for a way to follow.

In the search for approximate energies a mixed treatment is often adopted. This applies both to wavefunction and to density functional (DF) methods. The origin of this approach lies in the variety of physical effects to be taken care of. Finding density functionals which satisfy the Pauli principle is not a trivial task, although such functionals exist in principle [2]. The Kohn-Sham solution is to construct a Slater determinant (of course, satisfying the Pauli principle) which leads to the desired density, and is used to compute the (non-interacting) kinetic energy.[1] On the other hand, when applying the Kohn-Sham method, the remaining part of the energy is computed by relatively simple approximations, where only the density and the spin-density are present. One can find it surprising that the typically quantum-mechanical effects of exchange and correlation can be quite well described in this way.

In wavefunction methods it is inefficient to use the same approach for treating on the same level the near-degeneracy effects (present in the valence space) and the dynamical correlation (due to the short-range electron-electron interaction). For example, one can use a variational method for the first part, and perturbational one for the second (see, e.g.,[5]).

The present paper tries to show how such hybrid approaches can be used to produce new Kohn-Sham-like schemes. They all lose the extreme simplicity of the original method (and thus part of its attraction), but eliminate some of its shortcomings and in some cases also introduce a possibility of systematic improvement. Several programs manipulating multideterminantal wavefunctions are now available for atoms and molecules. The treatment is not prohibitive, as long as the number of Slater determinants and the size of the one-particle (orbital) basis sets are not too large.

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[1] It is sometimes stated that the orbitals in Kohn-Sham theory are only used to generate the density. This leads to a question which is sometimes asked in connection with Hartree theory [3]: 'Why are the orbitals chosen to be orthogonal?', showing that the Pauli principle is implicit in this treatment. Without orthogonal orbitals the energy would be minimized (for a given density) by choosing all orbitals equal (proportional to the square root of the density). The kinetic energy thus obtained would be that of von Weizsäcker (see, e.g., [4]), which yields poor energies in practice.

Spin-densities and on-top pair-densities

Some usual constrained-search definitions of the universal DFs ([6], see also [7]) are given below. The most general one, corresponding to the Hohenberg and Kohn idea [2] is

$$F[n] = < \Psi_n^{min} \mid \hat{T} + \hat{V}_{ee} \mid \Psi_n^{min} >$$

where $\hat{T}$ is the operator for the kinetic energy, $\hat{V}_{ee}$ is that for the electron-electron interaction, Ψ_n^{min} the antisymmetric wavefunction which minimizes $< \hat{T} + \hat{V}_{ee} >$ and yields the density n. The ground state energy can be found by minimizing (over n)

$$E[n] = F[n] + \int n v_{ext}$$

where v_{ext} is the external potential. The difficult task of finding an approximation to $F[n]$ can be simplified if the prescription of Kohn and Sham [1] is followed by decomposing it:

$$F[n] = < \Phi_n^{min} \mid \hat{T} \mid \Phi_n^{min} > + U[n] + E_{xc}[n] \tag{1}$$

Here Φ_n^{min} is the antisymmetric wavefunction which minimizes $< \hat{T} >$ and yields n. Please notice that Φ_n^{min} is a Slater determinant. Further,

$$U[n] = \frac{1}{2} \int n(\mathbf{r_1}) n(\mathbf{r_2}) \frac{1}{r_{12}} d^3r_1 d^3r_2 \tag{2}$$

Equation 1 defines $E_{xc}[n]$, the universal exchange-correlation DF which eventually has to be approximated. The universal correlation functional can be defined in a similar way:

$$E_c[n] = F[n] - (< \Phi_n^{min} \mid \hat{T} + \hat{V}_{ee} \mid \Phi_n^{min} >) \tag{3}$$

A fundamental step forward to the application of DFs consists in making the local density approximation (LDA), i.e. assuming that the functionals have the form

$$\int f(n(r)) d^3r \tag{4}$$

Here f is an arbitrary function which can be determined by doing uniform electron gas calculations. Often, a dependence of f on $\mid \nabla n \mid$ is also included. This produces LDA-like approximations, which may improve the results without changing the essentially local character of the approximation.

Significant progress in the construction of DFs was made by introducing the dependence of the universal functionals on a supplementary parameter, the spin-density, $n_\uparrow - n_\downarrow$ ($n_\uparrow$ and $n_\downarrow$ are the spin-up and spin-down densities, respectively) [8, 9]. Although this is not the only choice possible [10], it seems natural to use spin-densities, for obtaining the magnetization of materials, an information not available in the usual Hohenberg-Kohn theory (which yields the ground-state energy and density only). Furthermore, by replacing the functionals of the density by functionals of the density and the spin-density, more flexibility is introduced in the functionals, which finally leads to better numerical results. Equations 1 and 3 can then be re-written as:

$$F[n_\uparrow, n_\downarrow] =< \Phi^{min}_{n_\uparrow,n_\downarrow} \mid \hat{T} \mid \Phi^{min}_{n_\uparrow,n_\downarrow} > +U[n] + E_{xc}[n_\uparrow, n_\downarrow] \tag{5}$$

and

$$F[n_\uparrow, n_\downarrow] =< \Phi^{min}_{n_\uparrow,n_\downarrow} \mid \hat{T} + \hat{V}_{ee} \mid \Phi^{min}_{n_\uparrow,n_\downarrow} > +E_c[n_\uparrow, n_\downarrow] \tag{6}$$

where $\Phi^{min}_{n_\uparrow,n_\downarrow}$ is the Slater determinant which minimizes $< \hat{T} >$ and yields the partial densities $n_\uparrow$ and $n_\downarrow$. The couple $(n, n_\uparrow - n_\downarrow)$ has been replaced in the equations above by that of $(n_\uparrow, n_\downarrow)$ as: $n = n_\uparrow + n_\downarrow$.

While successful approximations to $E_{xc}[n_\uparrow, n_\downarrow]$ and $E_c[n_\uparrow, n_\downarrow]$ are available, there is a conceptual problem related to the use of these functionals. In the case of degeneracy (and of course the problem will appear in a related form in the case of near-degeneracy) different states have the same energy but might have different densities. It is very difficult to find an approximate DF which reproduces this feature of the exact one. The supplementary information given by the spin-density may even aggravate the problem, as one may have different degenerate states with the same density, but with different spin-densities.[2]

More explicitly, the spin-density is given by M_S times an M_S-invariant quantity (the 'normalized spin-density') [11]. In a triplet, for example, the state with $M_S = 0$ will have zero spin-density, although the normalized spin-density is the same as for the state with $M_S = 1$. Density functionals use, however, the spin-density and not the normalized spin-density. Thus DFs may lead to different energies for spin-densities which belong to a given

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[2] Let $\Psi(M_S)$ be one of the eigenstates (with $\hat{S}_z$ eigenvalue M_S), $\hat{n} = \sum \delta(r - r_i)$ the

multiplet, but yield different M_S. For such a case, the terms of a multiplet are not degenerate. A recipe to circumvent this problem is to argue that only one of the states can be computed (e.g. the one with maximal M_S). It will now be shown, that this prescription does not solve all the problems due to having different energies for the different terms of a multiplet. The example below intends to show that states with different M_S should be treated on the same footing, as there might be no way of picking out one of them.

Let us consider the dissociation of a molecule into two fragments in the case where a given spin state remains the ground state for all internuclear separations, from the equilibrium position to infinite separation. It may well happen that the dissociation products have different M_S. Examples of such a molecule is O_2 in the ${}^3\Sigma_g^-$ state, with $M_S = 1$ state dissociating into atoms in the ${}^3P$ state with $M_S = 1$ and $M_S = 0$ [12]. With LDA-like approximations non-degeneracy is artificially introduced for states with different M_S. In such a case two alternatives may be considered.

First, suppose that M_S is kept constant for all internuclear separations. This restriction on the Kohn-Sham determinant produces fragments with different M_S. One of the fragments will be in a state with an energy higher than the other because of the deficiencies of the LDA-like approximation. On the other hand, a calculation of the isolated fragment will chose the M_S state with the lowest energy. Thus, at infinite separation, the energy of the molecule will be higher than that of the isolated fragments. For the example mentioned above, let us suppose that the energy of the O atom is lower for $M_S = 1$ than that for $M_S = 0$. The energy of O_2 ($M_S = 1$) will be higher than that of two O atoms, each with $M_S = 1$. In conclusion, this first approach has shown not to respect size-consistency.

In the second approach, one can argue that DF theory is only for ground

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density operator, which commutes with the ladder operators $\hat{S}_+$ and $\hat{S}_-$; then

$$\begin{aligned}\frac{<\Psi(M_S)|\hat{n}|\Psi(M_S)>}{<\Psi(M_S)|\Psi(M_S)>} &= \frac{<\Psi(M_S)|\hat{n}|\hat{S}_+\hat{S}_-\Psi(M_S)>}{<\Psi(M_S)|\hat{S}_+\hat{S}_-\Psi(M_S)>} \\ &= \frac{<\hat{S}_-\Psi(M_S)|\hat{n}|\hat{S}_-\Psi(M_S)>}{<\hat{S}_-\Psi(M_S)|\hat{S}_-\Psi(M_S)>} \\ &= \frac{<\Psi(M_S-1)|\hat{n}|\Psi(M_S-1)>}{<\Psi(M_S-1)|\Psi(M_S-1)>}\end{aligned}$$

which shows that $\Psi(M_S)$ and $\Psi(M_S-1)$ yield the same density although they must yield different spin-densities, one integrating to $2M_S$, the other to $2(M_S-1)$.

states, and that energy optimization should be considered. Size-consistency can now be rescued, but one has to pay the price of the unphysical change of M_S at a certain internuclear separation. Even if apparently one may not be interested in the change of M_S, the latter indicates a change in the spin-density (which integrates to $M_S/2$) which is unphysical too, and would be usually interpreted as a change of 'magnetization'.

It may seem surprising, but the second choice seems to be closer to a solution towards escaping the dilemma mentionned above. In this case one asks if LDA-like approximations really produce spin-densities. In fact, a one-to-one correspondence between single-determinant spin-densities and on-top pair-densities suggests that it is the latter which really appears in usual density functional calculations. This correspondence was first used in calculations with correlation energy DFs [13]-[15] [3], later also in exchange-correlation density functionals [18]. A more detailed discussion of the new interpretation of spin-density functional calculations is given in [19]. Here only some significant features will be mentioned.

The pair-density (in the normalization of McWeeny [20]) is defined for any N-electron wavefunction Ψ by

$$P_2(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \sum_{\sigma_1,..,\sigma_N} \int d^3r_3 ... d^3r_N \mid \Psi \mid^2$$

The on-top pair-density is $P_2(\mathbf{r}, \mathbf{r})$. If the wavefunction is given by a single Slater determinant yielding spin-densities $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ the on-top pair-density is simply given by:

$$P_2(\mathbf{r}, \mathbf{r}) = 2 n_\uparrow(\mathbf{r}) n_\downarrow(\mathbf{r}) \tag{7}$$

Together with $n = n_\uparrow + n_\downarrow$, it means that the couple $(n_\uparrow, n_\downarrow)$ can be replaced for single-determinant functions by the couple (n, P_2), without loss of generality. First, $\Phi^{min}_{n_\uparrow, n_\downarrow}$ of equations 5 and 6 can be replaced by $\Phi^{min}_{n,P}$ the Slater determinant which minimizes $< T >$, yields the density n, and the on-top pair-density P_2. The conditions $P_2 \geq 0$ and $P_2 \leq n^2/2$ have to be imposed (as we consider Slater determinants, cf. eq. 7). Next, the dependence of the functionals E_{xc} and E_c on $n_\uparrow$ and $n_\downarrow$ can be substituted by the

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[3] The pair-density was probably first used with density functionals by Colle and Salvetti [16]. Please note that the equivalence of using pair-densities and spin-densities was also used in order to eliminate the dependence on the pair-density in favor of the spin-densities. [17]

dependence on n and P. Clearly, all Kohn-Sham calculations can be seen as being performed by using functionals which have the on-top pair-density as supplementary information (and not the spin-density).

The advantage of using P_2 instead of using the spin-density can be seen for example in the case of multiplets: as P_2 does not change with the change of the spin function [4] all terms of a multiplet will now have the same energy.

In the following some suggestions will be made, all based upon the idea of using more than a single Slater determinant. This requires a special consideration of the on-top pair-density. The energy of a system under consideration should be found by minimizing (now in a search over n and P_2)

$$E[n, P_2] = F[n, P_2] + \int n v_{ext} \tag{8}$$

When searching over P_2 the domain of allowed values has to be defined. While $P_2 \geq 0$ always holds, the condition used in the alternative interpretation of the Kohn-Sham equations, derived from Slater determinants ($P_2 \leq n^2/2$) is not satisfied by all types of wavefunctions.[5] The existence of such cases can be shown for P_2 of singlet states approximated by a wavefunction in which two electrons singly occupy different orbitals. (An example of such a singlet state is the ground state of Ce, [22].) Taking for simplification just two electrons and two orthogonal orbitals, χ_1 and χ_2, the wavefunction considered is

$$2^{-1/2}[\chi_1(1)\chi_2(2) + \chi_2(1)\chi_1(2)]$$

multiplied by a normalized spin-function. The density is

$$n = \mid \chi_1 \mid^2 + \mid \chi_2 \mid^2$$

and the on-top pair-density:

$$P_2 = 4 \mid \chi_1 \mid^2 \mid \chi_2 \mid^2$$

which can reach n^2 (at a point $\mathbf{r}$ where $\mid \chi_1(\mathbf{r}) \mid = \mid \chi_2(\mathbf{r}) \mid$).

In practice, the class of P_2 to be taken care of, does not pose a problem, as a wavefunction is used to construct both the density (as in a standard

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[4] Cf. footnote 2 showing the invariance of the density

[5] Slater determinants can be always used to generate any density and spin-density, derived from an antisymmetric wavefunction [21, 23]

Kohn-Sham calculation) and the on-top pair-density. Special care has to be taken, however, when defining the exchange-correlation or correlation functionals depending on n and P_2, as only Slater determinants are *usually* used for their parametrization, yielding values only for $0 \leq P_2 \leq n^2/2$. (For example, such functionals are obtained by using the ground state energies of the uniform electron gas with various degrees of polarization.) While it would be necessary to perform calculations for different systems (e.g. other states of the uniform electron gas), it is possible to choose the easy way: to extrapolate the results obtained for $0 \leq P_2 \leq n^2/2$ to $P_2 > n^2/2$ [18].[6]

It was mentioned above, that a Slater determinant is introduced in the expression of the kinetic energy, in order to enable finding simple approximations to the universal DF. In the following, a few suggestions will be made, how to extend this prescription, in the hope of finding better working density functionals. Another - and maybe more important motivation - is to find a way to a systematic improvement of results. For example the variational character of configuration interaction (CI) calculations, insures that the quality of the energy cannot be worsened by augmenting the set of Slater determinants used. As will be seen below, following this philosophy is also possible in the DF context, after extending the Kohn-Sham scheme.

Eigenfunctions of $\hat{S}^2$

The simplest generalization of the Kohn-Sham approach (which, however, does not allow a systematic improvement) is to require that Φ_n^{min} to be an eigenfunction of $\hat{S}^2$ (and not only of $\hat{S}_z$, as it is often done in practice):

$$F[n] =< \Phi_{n,S}^{min} \mid \hat{T} \mid \Phi_{n,S}^{min} > +U[n] + E_{xc,S}[n] \tag{9}$$

and

$$F[n] =< \Phi_{n,S}^{min} \mid \hat{T} + \hat{V}_{ee} \mid \Phi_{n,S}^{min} > -U[n] + E_{c,S}[n] \tag{10}$$

Here $\Phi_{n,S}^{min}$ is the antisymmetric wavefunction which minimizes $< \hat{T} >$, yields n and is an eigenfunction of $\hat{S}^2$ and $\hat{S}_z$. Note that now, the minimizing wavefunction is not necessarily a Slater determinant. The index S in $E_{xc,S}[n]$

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[6] Correlation energy functionals of n and P_2 have also been set equal to zero for $P_2 > n^2/2$ [13].

and $E_{c,S}[n]$ does not show a dependence on any specific eigenvalue of $\hat{S}^2$, but merely distinguishes these functionals from $E_{xc}[n]$ and $E_c[n]$ as defined previously.[7]

For a spin-independent Hamiltonian, the present approach does not restrict the generality of the Hohenberg-Kohn theorem. The exact ground state being an eigenfunction of $\hat{S}^2$, the minimum value of the DF will be the same as that obtained for the exact functional without the $\hat{S}^2$ restriction. Furthermore, as the Hamiltonian is spin-independent, there is no restriction on the universality of the DF.[8]

Extending $E_{xc,S}$ and $E_{c,S}$ to spin-density functionals leads to problems when a projected wavefunction $\Phi_{n,S}^{min}$ is used. For example, the ground state of the H_2 molecule has for each internuclear separation, R, $M_S = 0$. This condition is, of course, satisfied with the projected wavefunction which yields zero spin-density. For $R \to \infty$ the energy of two hydrogen atoms should be obtained. Even if the density is correct, the spin-density of two hydrogen atoms (each with $M_S = \pm 1/2$) would be non-zero. The dissociation energy obtained by following the potential curve, or by subtracting the energy of the isolated atoms from that of the molecule would be thus different. The difficulty mentioned here is, however, only apparent, if one considers that the DF depends not on the spin-density but on the on-top pair-density instead. In the preceding example of H_2, at large internuclear separations $P_2(\mathbf{r},\mathbf{r})$ tends to zero, as the probability of finding the two electrons around the same location $\mathbf{r}$ vanishes.

An universal functional can be thus constructed, using the density and the on-top pair-density. For exchange-correlation one has,

$$F[n, P_2] =< \Phi_{n,P_2,S}^{min} \mid \hat{T} \mid \Phi_{n,P_2,S}^{min} > +U[n] + E_{xc,S}[n, P_2], \tag{11}$$

while for correlation-only the equation is,

$$F[n, P_2] =< \Phi_{n,P_2,S}^{min} \mid \hat{T} + \hat{V}_{ee} \mid \Phi_{n,P_2,S}^{min} > +E_{c,S}[n, P_2]. \tag{12}$$

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[7] This difference would disappear in a local approximation using the uniform electron gas as a reference.

[8] Extending this approach from spin to spatial symmetry would lead to a difficulty. Allowing for any type of symmetry (as it was done above for spin symmetry) means that the group possessing only the identity must be included too; this is nothing but the ordinary case. On the other hand, having a dependence on the specific symmetry would violate the universality requirement of the DF. An alternative way is to build a DF for every symmetry [24].

Here $\Phi^{min}_{n,P_2,S}$ not only is the antisymmetric wavefunction which minimizes $< T >$, is an eigenfunction of $\hat{S}^2$ and yields the density $n(\mathbf{r})$ but also yields the on-top pair-density $P_2(\mathbf{r}, \mathbf{r})$.

Of course, the preceding equations do not contain a double-counting of the correlation energy, as the functionals $E_{xc,S}[n, P_2]$ and $E_{c,S}[n, P_2]$ are just defined by them. When the uniform spin-polarized electron gas is used to fix these functionals with the LDA ansatz the usual LDA expression will be obtained, because the electron gas states are eigenvalues of S^2 (cf. footnote 7). As one now has an approximation, correlation can be over- or underestimated. Some confusion may arise about introducing correlation by having more than one determinant appearing in Φ in the above formulas. It should be noticed, however, that for degenerate states the correlation energy often cannot be defined as the difference between that obtained with the exact (non-relativistic) wavefunction and the one obtained with a single determinant, as the latter often does not describe a specific state. This problem is avoided by using a reference of proper symmetry.

Another problem, related to the extension of the class of wavefunctions is the feasibility of calculations (which are straightforward with Slater determinants in usual Kohn-Sham calculations). For spin-projected Slater determinants formulas are available for the first- and second-order density matrices (see, e.g. [25]-[27]). With these formulas the only supplementary quantities needed are some spin-symmetry determined coefficients, which can be readily obtained. Thus the density, kinetic energy and on-top pair density can be obtained without significant supplementary effort.

There is still a need for a systematic numerical study of the present approach. Fig. 1 presents the potential curve for the H_2 molecule produced in a simplified non-self-consistent scheme [28]. First, an unrestricted single-determinant wavefunction was produced in a standard LDA calculations.[9] The energy was then recomputed for the projected wavefunction. The exchange-correlation functional used was dependent on the gradient of the density [31], but the spin-dependence was replaced by that on P_2 by using eq. 7. For small internuclear separations, the single determinant is an eigenfunction of $\hat{S}^2$. Thus no difference is to be noticed with respect to usual calculations. For larger separations, however, usual calculations tend to produce Slater determinants which break spin symmetry. Enforcing the latter produces a

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[9] The orbitals are numerical, produced by A. Becke's NUMOL [30].

lowering of the energy, improving the agreement with exact data [29].[10]

Extended orbital space

The wavefunction used in ordinary Kohn-Sham theory is a Slater determinant (cf. eqs. 5 and 6). This means that there are as many spin-orbitals as electrons. It is possible, however, to enlarge the orbital space in a systematic manner, allowing the construction of more than one Slater determinant within the space of spin-orbitals. For single-particle operators, like the kinetic energy, this supplementary freedom is not used (as a rule) and an alternative definition of the density functional (of the correlation energy) has to be used:

$$\tilde{F}[n, P_2] =< \tilde{\Phi}^{min}_{n,P_2} \mid \hat{T} + \hat{V}_{ee} \mid \tilde{\Phi}^{min}_{n,P_2} > + \tilde{E}_c[n, P_2]$$

$\tilde{\Phi}^{min}_{n,P_2}$ is the antisymmetric wavefunction which yields the density n, the on-top pair density P_2, minimizes $< \hat{T} + \hat{V}_{ee} >$ and is defined in a *reference space* (which can be defined in various ways, see below). As $\tilde{\Phi}^{min}_{n,P_2}$ is (except in the trivial case) more complex than the Hartree-Fock wavefunction, $\tilde{E}_c$ will describe a part of the correlation energy (that not obtainable in the reference space). Of course, the definition of the reference space must take care not to limit the universality of the density functional. Furthermore, the choice has to insure a high degree of transferability when approximations, like LDA, are made. For example, using a large space defined by a set of highly localized functions in the uniform electron gas, would leave an important part of the correlation energy to be described by $\tilde{E}_c$. On the other hand, the same space would allow a very good description of an atomic system. Transfering $\tilde{E}_c$ from the uniform electron gas to the atom would give an important contribution to the correlation energy both from the wavefunction part $< \tilde{\Phi}^{min}_{n,P_2} \mid \hat{T} + \hat{V}_{ee} \mid \tilde{\Phi}^{min}_{n,P_2} >$ and from $\tilde{E}_c$.

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[10] It may seem surprising at first sight that the energy is lowered by imposing a restriction on the wavefunction (that of being an eigenfunction of S^2). On the other hand, another restriction (that of having a single Slater determinant) has been lifted. The lowest eigenvalue of the Hamiltonian in the space of determinants needed to insure that the wavefunction is an eigenfunction of S^2 will be not higher than the expectation value of the Hamiltonian with any of the determinants.

Once the reference space is defined, the energy can be obtained by the usual minimization procedure,

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\begin{aligned}
E_{gs} &= \min_{n,P_2}\{F[n,P_2] + \int v_{ext} n\} \\
&= \min_{n,P_2}\{\min_{\tilde{\Phi}\to n,P_2} < \tilde{\Phi} \mid \hat{T} + \hat{V}_{ee} \mid \tilde{\Phi} > + \tilde{E}_c[n,P_2] + \int v_{ext} n\} \\
&= < \tilde{\Phi}^{min} \mid \hat{T} + \hat{V}_{ee} + V_{ext} \mid \tilde{\Phi}^{min} > + \tilde{E}_c[n(\tilde{\Phi}^{min}), P_2(\tilde{\Phi}^{min})] \quad (13)
\end{aligned}
$$

($\tilde{\Phi}$ is the wavefunction constructed in the reference space, and $\tilde{\Phi}^{min}$ is that obtained in the minimization procedure which also gives the final n and P_2).

Changing the size of the orbital space is a way to systematically improve the calculation: in the limit of the full orbital space $\tilde{E}_c$ goes to zero and the calculations to be performed using $\tilde{F}_c$ are full CI calculations, $\tilde{\Phi}^{min}$ being the full CI wavefunction. It should be noticed, however, that approximating $\tilde{E}_c$ usually destroys the upper bound property of the wavefunction calculation.

The arbitrariness of the choice of the orbital space leads to several schemes. One of them uses the space of natural orbitals with large occupation numbers [32]-[34]. The threshold separating the large from the small occupation numbers can be chosen freely, ensuring the required flexibility in the size of the orbital space.[11] The physics behind this approach is given by the fact that short-range correlations are described by orbitals with small occupation numbers (corresponding to large wavevectors $\mathbf{k}$ in the uniform electron gas) while near-degeneracy effects can be described by a the natural orbitals with large occupation numbers (with $\mathbf{k}$ up to a value lying not far above $\mathbf{k_F}$ in the uniform electron gas).

Another definition of the orbital space is obtained in analogy to a class of wavefunctions computations often quoted as the Complete Active Space Self-Consistent Field (CASSCF) method (see, e.g. [35]). In this definition all wavefunctions are generated within a space of $\tilde{N}$ ($\geq N$) spin-orbitals. Both the orbitals and the coefficients of the Slater determinants are chosen in order to minimize the energy. For a density functional, this leads to the minimization of $< \hat{T} + \hat{V}_{ee} >$ instead, for a given density (and possibly a given on-top pair-density). By enlarging $\tilde{N}$ (starting from N) it is possible

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[11] Numerical results show that a typical separation threshold is 0.01 atomic units for errors in the dissociation energies of diatomic molecules of 0.01 hartree. These values were obtained with E_c depending only on n (no dependence on P_2).

to produce the sequence of wavefunction calculations (the first one being of the Hartree-Fock type) insuring the possibility of improvement of the method [14, 36].

For local approximations, it is important to have a local measure of the orbital space. In the present context, one could choose for it [36]

$$m(\mathbf{r}) = \frac{\sum_{i=1}^{\tilde{N}} \mid \varphi_i(\mathbf{r}) \mid^2}{\sum_i^N \mid \varphi_i(\mathbf{r}) \mid^2}$$

where φ are the orbitals used, ordered after their appearance with increasing $\tilde{N}$.[12] $m(\mathbf{r})$ can take values between one and infinity. Thus $\tilde{F}[n, P_2]$ becomes

$$\tilde{F}[n, P_2, m] = < \tilde{\Phi}^{min}_{n,P_2,m} \mid \hat{T} + \hat{V}_{ee} \mid \tilde{\Phi}^{min}_{n,P_2,m} > + \tilde{E}_c[n, P_2, m]$$

where $\tilde{\Phi}^{min}_{n,P_2,m}$ is the antisymmetric wavefunction minimizing $< \hat{T} + \hat{V}_{ee} >$ in the space of $\tilde{N}$ orbitals yielding n, P_2 and m. The existence of a wavefunction producing n, P_2 and m is guaranteed by construction (cf. eq. 13). Furthermore, any m can be produced in homogeneous electron gas calculations as it is given in this case by the ratio of a maximal $\mathbf{k}$ to $\mathbf{k_F}$ to the third power.

A few applications have been performed by using for E_c the approximation:

$$E_c \approx \int \phi(n, m) f(n_\uparrow, n_\downarrow, \mid \nabla n_\uparrow \mid, \mid \nabla n_\downarrow \mid)$$

Here ϕ is a factor that includes the dependence on $m(\mathbf{r})$. It is equal to one for $\tilde{N} = N$ and decreases as $\tilde{N}$ becomes larger; $m \to 0$ for $\tilde{N} \to \infty$. The function m used is obtained from unpolarized uniform electron gas calculations. For $f(n_\uparrow, n_\downarrow, \mid \nabla n_\uparrow \mid, \mid \nabla n_\downarrow \mid)$ the expression of Vosko et al. [37] was used for the local part, and the gradient correction was taken from [38]. The quantities $n_\uparrow, n_\downarrow, \mid \nabla n_\uparrow \mid, \mid \nabla n_\downarrow \mid$ appearing in f are not spin-densities, but were constructed from n and P_2 (cf. eq. 7). The CASSCF calculations were done with the program Molpro [39].

Fig. 2 shows the results of a series of calculations on He and Ne^{8+} using this method [14]. The two curves on the lower half of the picture show the

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[12] It should be noticed that the orbitals change with $\tilde{N}$. It is possible, however, to follow the orbitals from one calculation to the other, e.g. by symmetry or computing the overlaps. In fact, the orbitals from the calculation with smaller $\tilde{N}$ can be used as starting orbitals in the calculation with larger $\tilde{N}$.

errors of the pure wavefunction (CASSCF) calculation.[13] The upper half of the figure shows the errors present after addition of the DF to the CASSCF energy. The value obtained in the space of only one orbital is, of course, at the Hartree-Fock level. While the DF correlation energy (with $\phi = 1$) yields a good energy for He, the error made for Ne^{8+} is nearly as large as without DF (but of opposite sign). When the orbital space is increased, the error remains small for He, and decreases for Ne^{8+}. [14]

Splitting of the electron-electron interaction

The physical background for a transfer of density functionals in LDA-like approximations seems to rely on the transferability of short-range electron-electron interactions. This can be studied explicitly by splitting the operator $\hat{V}_{ee}$ into a short-range ($\hat{V}_s$) and a long-range ($\hat{V}_l$) part:

$$\hat{V}_{ee} = \hat{V}_s + \hat{V}_l$$

This separation can be done in position space, for example with a Yukawa-like potential:

$$\hat{V}_s = \sum_{i<j} v_s(i,j) \tag{14}$$

$$v_s(i,j) = \frac{e^{-\mu r_{ij}}}{r_{ij}}$$

where r_{ij} is the interelectronic distance. Alternatively, such a splitting can be done in momentum space, for example by using a momentum which defines the separation of large from small values. Both types of definitions are common in physics (see, e.g., [40, 41]) and a few suggestions have been made to use only the short-range part of $\hat{V}_{ee}$ for the transfer of LDA-like density functionals (see, e.g., [42, 43]). Naturally, the remaining part of $\hat{V}_{ee}$ will contribute to the energy, and there is a need of a method well-suited for

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[13] An error of ≈ 1 mhartree remains even for the maximal $\tilde{N}$ which can be attained in the basis set used here; in particular, orbitals with higher angular momentum are missing.

[14] A comparison with the results presented in [32] shows that the error is small with just one orbital in the wavefunction calculation. This is due to the choice of the threshold which uses the information about the largest occupation number not used in the wavefunction calculation.

long-range interactions [44, 45]. Recently some progress has been done along these lines [46]. It is possible to define functionals for short-range exchange and correlation (or correlation only)

$$E_{s,xc}[n] = F[n] - (< \Phi_n^{min,l} \mid \hat{T} + \hat{V}_l \mid \Phi_n^{min,l} > + U_s[n])$$

$$E_{s,c}[n] = F[n] - (< \Phi_n^{min,l} \mid \hat{T} + \hat{V}_l \mid \Phi_n^{min,l} > + < \Phi_n^{min} \mid \hat{V}_s \mid \Phi_n^{min} >)$$

where

$$U_s[n] = \frac{1}{2} \int n(\mathbf{r_1}) n(\mathbf{r_2}) v_s(\mathbf{r_1}, \mathbf{r_2}) d^3 r_1 d^3 r_2$$

$\Phi_n^{min,l}$ is the antisymmetric wavefunction yielding n and minimizing $< \hat{T} + \hat{V}_l >$. The analogy to eqs. 1 and 3 is evident: here $\hat{T}$ has been replaced by $< \hat{T} + \hat{V}_l >$. The ground state energy, can be obtained by minimizing over all antisymmetric wavefunctions Φ:

$$\begin{aligned} E_{gs} &= \min_n (F[n] + \int n v_{ext}) \\ &= \min_\Phi (< \Phi \mid \hat{T} + \hat{V}_l \mid \Phi > + \int n(\Phi) v_{ext} + U_s[n(\Phi)] + E_{s,xc}[n(\Phi)]) \\ &= \min_\Phi (< \Phi \mid \hat{T} + \hat{V}_l \mid \Phi > + \int n(\Phi) v_{ext} + < \Phi_n^{min} \mid \hat{V}_s \mid \Phi_n^{min} > + E_{s,c}[n(\Phi)]) \end{aligned}$$

As the choice of $\hat{V}_s$ ($\hat{V}_l$) remains arbitrary, it is possible to switch from the usual Kohn-Sham case ($\hat{V}_s = \hat{V}_{ee}, \hat{V}_l = 0$) to the usual wavefunction (full configuration interaction) calculation ($\hat{V}_s = 0, \hat{V}_l = \hat{V}_{ee}$). For example, by choosing a Yukawa-type interaction for $\hat{V}_s$ (cf. eq. 14), it is possible to change continuously the exponential parameter from zero to infinity, allowing for a smooth tuning of the separation in the Hamiltonian. The local approximation (eq. 4) can be made for $E_{xc,s}$ and for $E_{c,s}$ by using uniform electron gas data. While the formula for the exchange energy per particle can be obtained analytically,

$$\epsilon_{x,s} = -\frac{2}{\pi} k_F \left(\frac{3}{8} - a \, tan^{-1} \frac{1}{a} + \frac{3 + a^2}{4} a^2 \, ln \frac{1 + a^2}{a^2} - \frac{a^2}{4} \right)$$

where $a = \mu/(2k_F)$ and $k_F = (3\pi^2 n)^{1/3}$, a numerical computation is needed for the correlation energy. Such a calculation was performed in the coupled-cluster approximation, changing only the electron-electron interaction in the formulas of Ref. [47]. The results of this calculation can be found in the Table.

Fig. 3. shows the energy errors obtained within the local approximation for Yukawa-like interaction, at different values of the exponential parameter μ, for the He atom.[15] The curve shows the results obtained with $E_{xc,s}$. (An analogous trend is observed when $E_{c,s}$ is used, cf. Ref. [46]). The error rapidly drops off with increasing μ from 0 (corresponding to an usual LDA calculation) to $\mu \approx 2$. Beyond this value practically no change can be noticed in the energy. A possible explanation for this behavior might be that $\mu \approx 2$ is already large enough to exclude all DF contributions. In other words, one already obtains a pure variational wavefunction calculation.

Fig. 4 shows, however, that this hypothesis is wrong: the error in the energy is clearly much smaller than the DF contributions for $\mu = 2$ ($E_{xc,s} =$ 0.274 hartree, and $E_{c,s} = 0.046$ hartree). In fact, it turns out that much higher values of μ are needed to approach the full wavefunction calculation and to switch off the DF contributions.

The example of the He atom shows that the short-range interaction can be transfered from the uniform electron gas. At the same time it illustrates how a systematic control of the computation is possible: one simply has to repeat the calculation with a larger μ, and check the stability of the result. Of course, experience can replace this check, as it often does in other calculations. Present experience seems to show that (for neutral systems) $\mu \approx 2$ is a good compromise for good accuracy and a maximum DF contribution. Experience must also show how much effort is needed to obtain the minimizing wavefunction (which now is not a single Slater determinant). Usually the need of large basis sets is attributed to the pole in $\hat{V}_{ee}$ for $R_{ij} \to 0$ (see, e.g. [48]). This behavior can be eliminated in $\hat{V}_l$, however, as can be seen, for example, by analyzing the Yukawa potential. One thus can be optimistic about the application of this approach.

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[15] Technical details are as in Ref. [46], with the exception of the functional given in Table 1. The role of the electron gas calculation (of Fermi hypernetted chain type in Ref. [46]) is only marginal.

Conclusions

By introducing a wavefunction into the universal density functional Kohn and Sham have considerably simplified the search for approximations of the universal DFs. In other words, certain features are more easily described by a wavefunction than by LDA-like DFs. While the main feature introduced by the Slater determinant of Kohn and Sham is antisymmetry, there are probably also other properties which are taken care of more easily by wavefunctions than by DFs, for example spin symmetry properties or near-degeneracy effects. In order to treat these, more than a single Slater determinant is often needed, which in turn requires extending the original Kohn-Sham formalism. A few of these possibilities have been presented in this chapter.

Another advantage of extending the Kohn-Sham formalism to a number of Slater determinants is the possibility of generating a practical scheme allowing systematic improvement in the meaning used in wavefunction calculations: a sequence of calculations which are expected to yield better and better results. For the prescriptions presented here there is - as always - a higher price to pay for a better quality. Nevertheless, as DFs are well suited to transfer the effects due to short-range interaction between electrons, adding them should considerably reduce the effort with respect to pure multideterminant wavefunction calculations.

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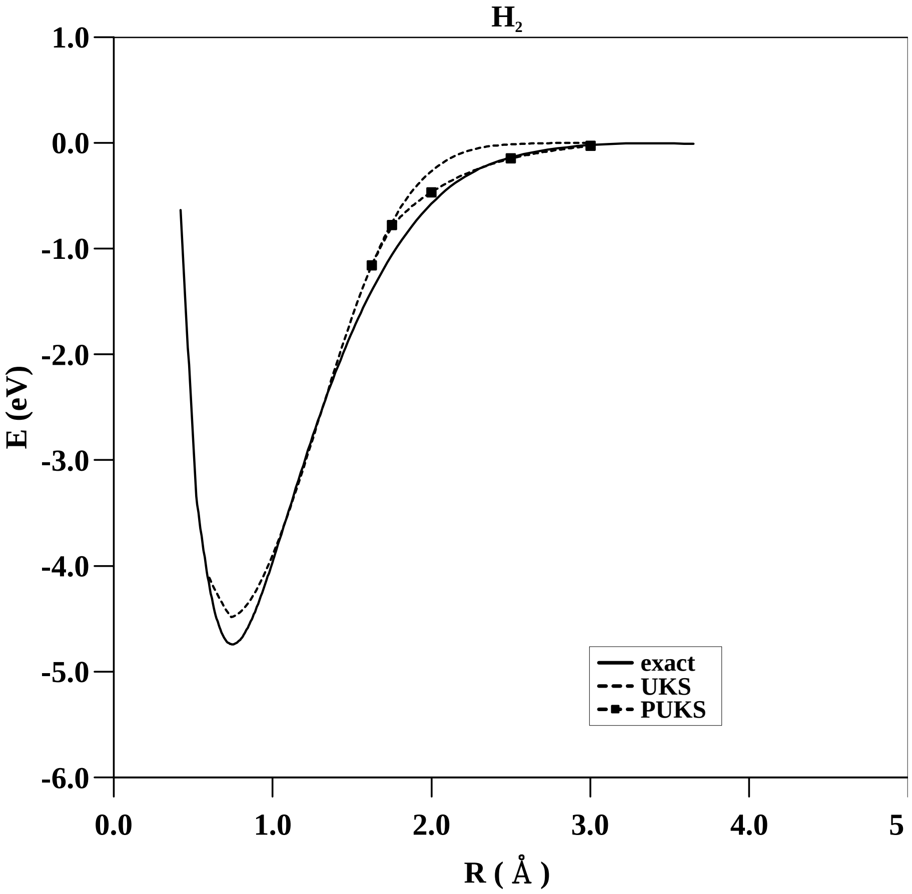

Figure 1. Potential curve for the hydrogen molecule obtained within usual (unrestricted) Kohn-Sham calculations (UKS) and after projection to proper spin symmetry (PUKS [28]). The exact potential curve [29] is also shown.

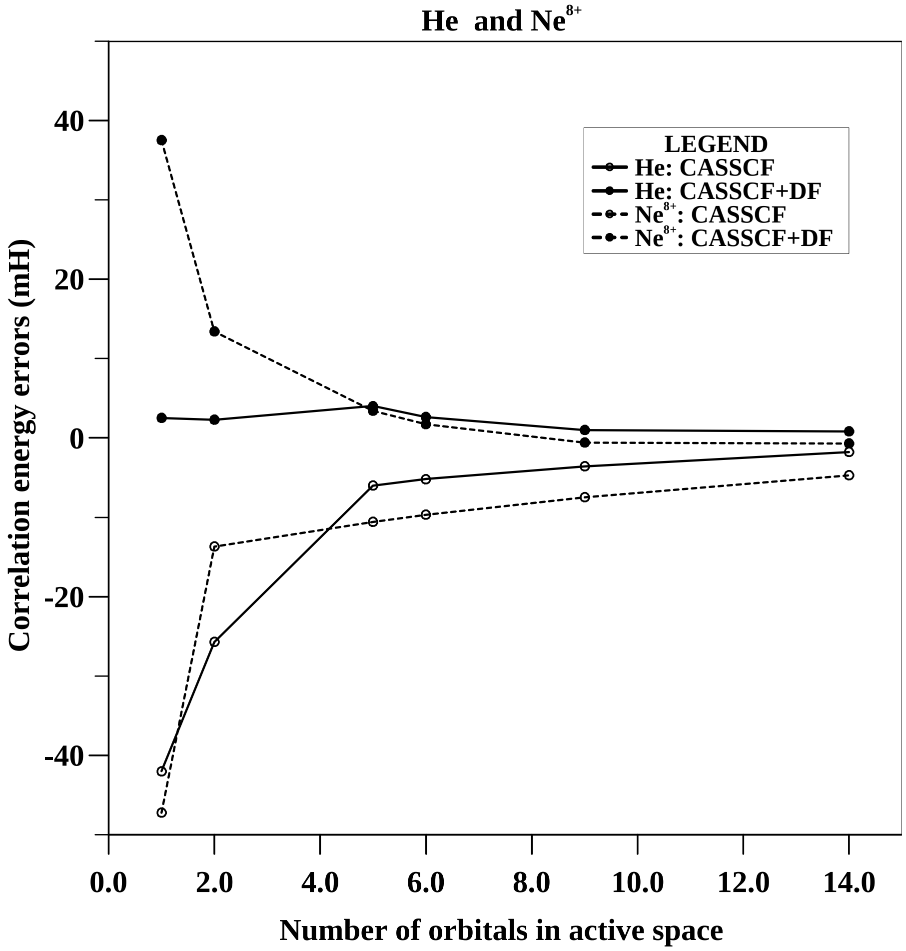

Figure 2. Errors of CASSCF (open circles, lower half of the figure) and CASSCF+DF (full circles, upper half of the figure) calculations for different size of the orbital space; for He (full lines) and Ne^{8+} (dashed lines) [14]. When only one orbital is present, the result obtained corresponds to the Kohn-Sham calculation with pure correlation energy functional. For two orbitals a second s orbital has been added; this is followed by the addition of a set of p orbitals, a third s orbital, a second set of p orbitals, the last point shown corresponding obtained by finally adding a set of d orbitals.

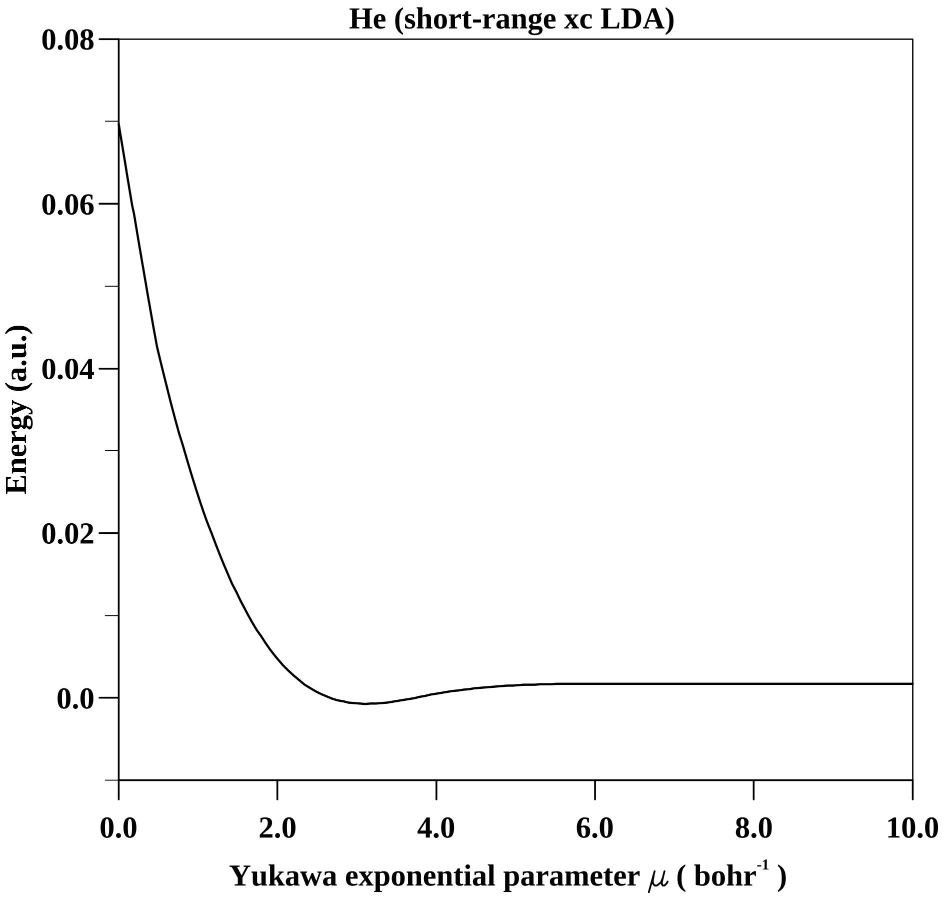

Figure 3. Energy difference between the calculated (local density approximation for Yukawa short-range electron-electron interaction) and 'exact' total energies with density functionals for exchange and correlation for the He atom, as a function of the Yukawa exponential factor; in atomic units.

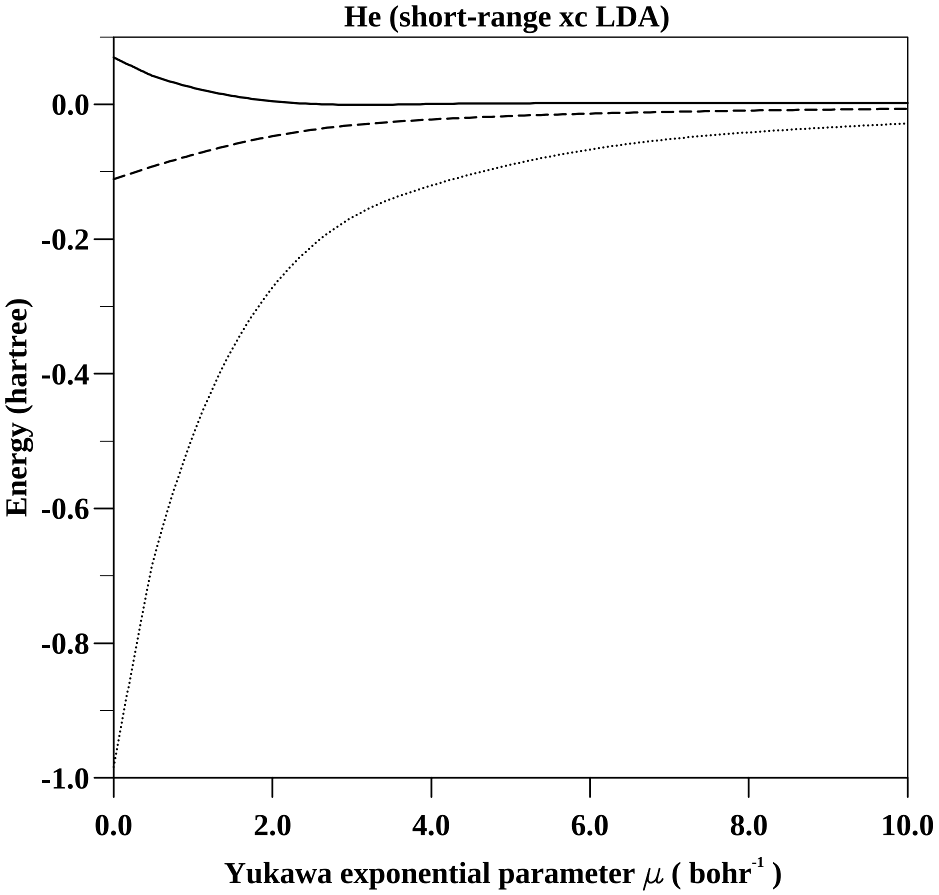

Figure 4. Error in the total energy of the He atom calculation (full curve, cf. Fig.3) compared with the exchange-correlation (dotted curve) and with the correlation (dashed curve) contributions to the energy; as functions of the Yukawa exponential parameter (exchange-correlation DF)

Table. Ratio between the short-range correlation energy and the total correlation energy of a uniform electron gas, obtained in a coupled-cluster calculation of the uniform electron gas with Yukawa-type interaction ($r_s = [3/(4\pi n)]^{1/3}$, μ is the Yukawa exponent in eq. 14, in atomic units).

r_s μ	0.2	0.5	1.0	2.0	3.0	4.0	5.0	6.0	10.0
0.0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.2	0.992	0.976	0.950	0.894	0.836	0.781	0.730	0.682	0.535
0.5	0.966	0.916	0.835	0.690	0.573	0.483	0.414	0.361	0.231
1.0	0.914	0.806	0.655	0.446	0.325	0.250	0.201	0.165	0.093
2.0	0.809	0.615	0.409	0.221	0.142	0.101	0.076	0.060	0.031
3.0	0.713	0.475	0.273	0.130	0.079	0.053	0.039	0.029	0.015
4.0	0.631	0.373	0.195	0.085	0.050	0.033	0.023	0.017	0.008
5.0	0.559	0.298	0.145	0.060	0.034	0.022	0.016	0.012	0.005
6.0	0.498	0.244	0.113	0.044	0.026	0.016	0.011	0.008	0.003
7.0	0.445	0.202	0.090	0.034	0.019	0.013	0.009	0.006	0.003
8.0	0.400	0.171	0.073	0.027	0.015	0.009	0.005	0.004	0.003
9.0	0.360	0.146	0.060	0.021	0.012	0.008	0.005	0.004	0.003
10.0	0.326	0.126	0.051	0.018	0.011	0.006	0.004	0.002	0.003
11.0	0.296	0.110	0.043	0.016	0.008	0.005	0.004	0.002	0.000
12.0	0.270	0.097	0.038	0.014	0.008	0.005	0.002	0.002	0.000
13.0	0.247	0.086	0.033	0.011	0.007	0.003	0.002	0.002	0.000
14.0	0.227	0.077	0.029	0.010	0.005	0.003	0.002	0.002	0.000
15.0	0.209	0.069	0.025	0.009	0.005	0.003	0.002	0.000	0.000
16.0	0.193	0.062	0.023	0.008	0.004	0.003	0.002	0.000	0.000
17.0	0.179	0.057	0.020	0.007	0.004	0.003	0.002	0.000	0.000
18.0	0.167	0.051	0.019	0.006	0.004	0.002	0.002	0.000	0.000
19.0	0.155	0.047	0.017	0.006	0.004	0.002	0.000	0.000	0.000
20.0	0.145	0.043	0.015	0.005	0.003	0.002	0.000	0.000	0.000
21.0	0.135	0.040	0.014	0.005	0.003	0.002	0.000	0.000	0.000
22.0	0.127	0.037	0.013	0.005	0.003	0.002	0.000	0.000	0.000
23.0	0.119	0.034	0.012	0.003	0.003	0.002	0.000	0.000	0.000
24.0	0.113	0.032	0.011	0.003	0.003	0.002	0.000	0.000	0.000