

## System-adapted correlation energy density functionals from effective pair interactions

P. GORI-GIORGI\* and A. SAVIN

Laboratoire de Chimie Théorique, CNRS, Université Pierre et Marie Curie,  
4 Place Jussieu, F-75252 Paris, France

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This article discusses some ideas concerning an ‘average-pair-density functional theory’, in which the ground-state energy of a many-electron system is rewritten as a functional of the spherically and system-averaged pair density. These ideas are further clarified with simple physical examples. Then it is shown that the proposed formalism can be combined with density functional theory to build system-adapted correlation energy functionals. A simple approximation for the unknown effective electron–electron interaction that enters in this combined approach is described, and results for the He series and for the uniform electron gas are briefly reviewed.

### 1. Introduction

Density Functional Theory (DFT) is nowadays the most widely used method for the calculation of electronic structure in both solid-state physics and quantum chemistry [1–3]. The accuracy of the results coming from a DFT calculation is limited by the approximate nature of the exchange and correlation energy  $E_{xc}[n]$  and the associated potential, its functional derivative. While, at present, many algorithms for a very accurate or even exact exchange potential  $v_x(\mathbf{r})$  and energy  $E_x[n]$  are available [3, 4], better approximations for calculating accurate correlation energies  $E_c[n]$  are still needed.

In a recent paper [5], we proposed an alternative approach to build the DFT correlation energy  $E_c[n]$ . The method consists in solving simple radial equations to generate the spherically and system-averaged pair density (APD)  $f(r_{12})$  along the so-called adiabatic connection. Besides its practical use for DFT, we realized that this method has many aspects that deserve to be better investigated, including the possibility for an alternative theory completely based on  $f(r_{12})$ . In this work, we sketch the basic ideas for this alternative theory, further we discuss them with simple physical examples, and deal with some of the aspects that went overlooked in [5]. The scope of this paper is to lay the foundations for an approach that will be further

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\*Corresponding author. Email: gp.giorgi@caspur.it

developed towards the construction of a self-consistent scheme combining the radial equations for  $f(r_{12})$  with the Kohn–Sham (KS) equations.

The paper is organized as follows. After defining the notation, we develop in section 3 the formalism corresponding to a theory based on the spherically and system-APD, reviewing at the same time the corresponding concepts for DFT. We hope that this parallel treatment will make it easier for the reader to familiarize with the new concepts. We then give, in section 4, some simple physical examples. Section 5 is devoted to explain how the ideas of section 3 can be used to build correlation energy functionals for DFT. A simple, physically motivated, approximation for the unknown effective electron–electron (e–e) interaction that appears in the formalism is discussed in section 6, where applications to two-electron atoms and to the uniform electron gas are also briefly reviewed. The last section is devoted to conclusions and perspectives.

## 2. Definitions

We start from the standard  $N$ -electron Hamiltonian (in Hartree atomic units,  $\hbar = m = a_0 = e = 1$ , used throughout)

$$H = T + V_{ee} + V_{ne}, \quad (1)$$

$$T = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2, \quad (2)$$

$$V_{ee} = \frac{1}{2} \sum_{i \neq j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (3)$$

$$V_{ne} = \sum_{i=1}^N v_{ne}(\mathbf{r}_i), \quad (4)$$

where  $v_{ne}$  is the external potential due to nuclei. Given  $\Psi$ , the ground-state wavefunction of  $H$ , we consider two reduced quantities that fully determine, respectively, the expectation values  $\langle \Psi | V_{ne} | \Psi \rangle$  and  $\langle \Psi | V_{ee} | \Psi \rangle$ , i.e. the usual one-electron density

$$n(\mathbf{r}) = N \sum_{\sigma_1 \dots \sigma_N} \int |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N, \quad (5)$$

and the spherically and system-APD, which is obtained as an integral of  $|\Psi|^2$  over all variables but  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ ,

$$f(r_{12}) = \frac{N(N-1)}{2} \sum_{\sigma_1 \dots \sigma_N} \int |\Psi(\mathbf{r}_{12}, \mathbf{R}, \mathbf{r}_3, \dots, \mathbf{r}_N)|^2 \frac{d\Omega_{\mathbf{r}_{12}}}{4\pi} d\mathbf{R} d\mathbf{r}_3 \dots d\mathbf{r}_N, \quad (6)$$

where  $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ , and  $\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$ . The function  $f(r_{12})$  is also known in chemistry as intracule density [6–12], and, when multiplied by the volume element  $4\pi r_{12}^2 dr_{12}$ , is proportional to the probability distribution for the e–e distance.

We then have

$$\langle \Psi | V_{\text{ne}} | \Psi \rangle = \int n(\mathbf{r}) v_{\text{ne}}(\mathbf{r}) d\mathbf{r} \quad (7)$$

$$\langle \Psi | V_{\text{ee}} | \Psi \rangle = \int \frac{f(r_{12})}{r_{12}} d\mathbf{r}_{12} = \int_0^\infty \frac{f(r_{12})}{r_{12}} 4\pi r_{12}^2 dr_{12}. \quad (8)$$

In the following text we also deal with modified systems in which the external potential and/or the e–e interaction is changed. Thus, the notation  $V_{\text{ee}}$  and  $V_{\text{ne}}$  will be used to characterize the physical system, while the modified systems will be defined by  $W$  and  $V$ , with

$$W = \frac{1}{2} \sum_{i \neq j}^N w(|\mathbf{r}_i - \mathbf{r}_j|), \quad (9)$$

$$V = \sum_{i=1}^N v(\mathbf{r}_i), \quad (10)$$

where the pairwise interaction  $w$  always depends only on  $|\mathbf{r}_i - \mathbf{r}_j|$ .

### 3. Formalism

In this section we present an ‘APD-functional theory’ (APDFT) based on the function  $f(r_{12})$  highlighting, step-by-step, the analogies in reasoning with the derivation of standard DFT.

#### 3.1. DFT – the universal functional

In standard DFT one defines a universal functional of the one-electron density  $n$  as resulting from a constrained search over all the antisymmetric wavefunctions  $\Psi$  that yield  $n$  [13]

$$\tilde{F}[n; V_{\text{ee}}, T] = \min_{\Psi \rightarrow n} \langle \Psi | T + V_{\text{ee}} | \Psi \rangle, \quad (11)$$

or, more completely, as a Legendre transform [14]

$$F[n; V_{\text{ee}}, T] = \sup_v \left\{ \min_{\Psi} \langle \Psi | T + V_{\text{ee}} + V | \Psi \rangle - \int n(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \right\} \quad (12)$$

In both equations (11) and (12), the dependence on the e–e interaction (and on the kinetic energy operator  $T$ ) has been explicitly shown in the functional. The universality of the functional  $F$  stems exactly from the fact that the e–e interaction is always  $1/r$  (and that  $T$  is always the same).

The ground-state energy  $E_0$  of the system can then be obtained by minimizing the energy with respect to  $n$ ,

$$E_0 = \min_n \left\{ F[n; V_{\text{ee}}, T] + \int n(\mathbf{r}) v_{\text{ne}}(\mathbf{r}) d\mathbf{r} \right\}. \quad (13)$$

### 3.2. APDFT – the system-dependent functional

Similarly, we can define a system-dependent functional (i.e. a functional depending on the external potential  $V_{\text{ne}}$ , and thus on the specific system) of the APD  $f(r_{12})$  as

$$\tilde{G}[f; V_{\text{ne}}, T] = \min_{\Psi \rightarrow f} \langle \Psi | T + V_{\text{ne}} | \Psi \rangle, \quad (14)$$

or better as

$$G[f; V_{\text{ne}}, T] = \sup_w \left\{ \min_{\Psi} \langle \Psi | T + W + V_{\text{ne}} | \Psi \rangle - \int f(r_{12}) w(r_{12}) dr_{12} \right\}. \quad (15)$$

The ground-state energy can be obtained by a minimization with respect to  $f$

$$E_0 = \min_f \left\{ G[f; V_{\text{ne}}, T] + \int \frac{f(r_{12})}{r_{12}} d\mathbf{r}_{12} \right\}. \quad (16)$$

Evidently, with respect to DFT, the functional  $G$  has the disadvantage of being not universal: in DFT, an approximation for  $F$  should be in principle valid for all systems. However, the crucial point for applications is understanding how difficult it is to build a reasonable approximation for  $G[f; V_{\text{ne}}, T]$ , given a certain  $V_{\text{ne}}$ . In the particular combination of DFT and APDFT presented in section 5 the lack of universality of  $G$  is not an issue.

Another issue concerns the  $N$ -representability conditions on  $f(r_{12})$ , i.e. which constraints must a given  $f$  satisfy to guarantee that it comes from the contraction of an  $N$ -electron wavefunction  $\Psi$ . This is a problem shared with other generalizations of DFT, like the pair-density functional theory [15–19]. The  $N$ -representability conditions of  $f(r_{12})$  are evidently related to those on the pair density, and we thus might expect that they are not a trivial matter [19]. The definition of the functional  $G$  of equation (15) formally overcomes the  $N$ -representability problem by giving a divergent ( $+\infty$ ) answer for any non- $N$ -representable  $f$  (when  $f$  is not  $N$ -representable the right-hand side of equation (15) is not bounded from above), but this is not a practical solution when coming to applications. As we shall see, in the particular use of APDFT presented in section 5, this issue is not particularly crucial from a practical point of view, since we use APDFT to build correlation functionals for DFT.

### 3.3. DFT – adiabatic connection

In DFT, one usually defines a set of Hamiltonians depending on a parameter  $\lambda$  [20–22],

$$H^\lambda = T + W^\lambda + V^\lambda, \quad (17)$$

having all the same one-electron density, equal to the one of the physical system

$$n^\lambda(\mathbf{r}) = n(\mathbf{r}) \quad \forall \lambda. \quad (18)$$

If  $W^{\lambda=0} = 0$  and  $W^{\lambda_{\text{phys}}} = V_{\text{ee}}$ , one switches continuously from a non-interacting system to the physical system, while keeping the density fixed by means of a suitable external potential  $V^\lambda$ . Obviously, the APD  $f(r_{12})$  changes with  $\lambda$ . By the Hellmann–Feynmann theorem,

$$\frac{\partial E_0^\lambda}{\partial \lambda} = \left\langle \Psi^\lambda \left| \frac{\partial W^\lambda}{\partial \lambda} + \frac{\partial V^\lambda}{\partial \lambda} \right| \Psi^\lambda \right\rangle = \int f^\lambda(r_{12}) \frac{\partial w^\lambda(r_{12})}{\partial \lambda} \, d\mathbf{r}_{12} + \int n(\mathbf{r}) \frac{\partial v^\lambda(\mathbf{r})}{\partial \lambda} \, d\mathbf{r}, \quad (19)$$

so that by directly integrating equation (19), and by combining it with equation (13), one obtains

$$F[n; V_{\text{ee}}, T] = T_s[n] + \int_0^{\lambda_{\text{phys}}} d\lambda \int d\mathbf{r}_{12} f^\lambda(r_{12}) \frac{\partial w^\lambda(r_{12})}{\partial \lambda}, \quad (20)$$

where  $T_s[n]$  is the kinetic energy of a non-interacting system of  $N$  electrons with density  $n(\mathbf{r})$ .

More generally, one can be interested in using as a starting point a system of partially interacting electrons, corresponding to a particular value of the coupling  $\lambda$  (say,  $\lambda = \mu$ ) between 0 and  $\lambda_{\text{phys}}$ . In this case, if  $\Psi^\mu$  is the wavefunction of the system with partial interaction  $W^\mu$  (and external potential  $V^\mu$ ) we have

$$F[n; V_{\text{ee}}, T] = \langle \Psi^\mu | T + W^\mu | \Psi^\mu \rangle + \int_\mu^{\lambda_{\text{phys}}} d\lambda \int d\mathbf{r}_{12} f^\lambda(r_{12}) \frac{\partial w^\lambda(r_{12})}{\partial \lambda}. \quad (21)$$

Usually, the adiabatic connection is performed along a linear path by setting  $W^\lambda = \lambda V_{\text{ee}}$  (thus  $\lambda_{\text{phys}} = 1$ ), but some non-linear choices can be more convenient when dealing with approximations.

### 3.4. APDFT – adiabatic connection

We can also define a set of Hamiltonians

$$H^\xi = T + W^\xi + V^\xi, \quad (22)$$

in which the function  $f(r_{12})$  is kept fixed, equal to the one of the physical system,

$$f^\xi(r_{12}) = f(r_{12}) \quad \forall \xi, \quad (23)$$

If  $V^{\xi=0} = 0$  and  $V^{\xi_{\text{phys}}} = V_{\text{ee}}$ , we are switching continuously from a system of  $N$  free electrons interacting with a modified potential  $w^{\xi=0}(r_{12})$ , to the physical system. That is,  $f(r_{12})$  is kept fixed as  $\xi$  varies by means of a suitable e–e interaction  $W^\xi$  while the one-electron density  $n(\mathbf{r})$  changes with  $\xi$ . Again, by the Hellmann–Feynmann

theorem, we find

$$\frac{\partial E_0^\xi}{\partial \xi} = \left\langle \Psi^\xi \left| \frac{\partial W^\xi}{\partial \xi} + \frac{\partial V^\xi}{\partial \xi} \right| \Psi^\xi \right\rangle = \int f(r_{12}) \frac{\partial w^\xi(r_{12})}{\partial \xi} d\mathbf{r}_{12} + \int n^\xi(\mathbf{r}) \frac{\partial v^\xi(\mathbf{r})}{\partial \xi} d\mathbf{r}, \quad (24)$$

so that

$$G[f; V_{\text{ne}}, T] = T_{\text{f}}[f] + \int_0^{\xi_{\text{phys}}} d\xi \int d\mathbf{r} n^\xi(\mathbf{r}) \frac{\partial v^\xi(\mathbf{r})}{\partial \xi}, \quad (25)$$

where  $T_{\text{f}}[f]$  is the kinetic energy of a system of  $N$  free fermions (zero external potential) having the same  $f(r_{12})$  of the physical system. A simple example of such adiabatic connection is given in section 4.1. As we shall see, given a confined physical system, the corresponding  $w^{\xi=0}(r_{12})$  must be partially attractive (in order to create a bound cluster of fermions). This could in principle lead to ‘exotic’ ground states for some of the systems corresponding to  $\xi < \xi_{\text{phys}}$ . This issue is not considered in this paper, and shall be investigated in future work.

Similarly to the DFT case, it could be convenient to choose as starting point a system with an external potential corresponding to some coupling constant  $\xi$  (say,  $\xi = \alpha$ ) between 0 and  $\xi_{\text{phys}}$ . If  $\Psi^\alpha$  is the ground-state wavefunction of the system with external potential  $V^\alpha$  (and e–e interaction  $W^\alpha$ ) we have

$$G[f; V_{\text{ne}}, T] = \langle \Psi^\alpha | T + V^\alpha | \Psi^\alpha \rangle + \int_\alpha^{\xi_{\text{phys}}} d\xi \int d\mathbf{r} n^\xi(\mathbf{r}) \frac{\partial v^\xi(\mathbf{r})}{\partial \xi}. \quad (26)$$

### 3.5. DFT – Kohn–Sham equations

One-particle equations in DFT can be obtained by defining a set of orthogonal orbitals  $\varphi_i(\mathbf{r})$  with occupation number  $v_i$  that minimize  $\sum_i v_i \langle \varphi_i | -\frac{1}{2}\nabla^2 | \varphi_i \rangle$  and yield the density of the physical system,  $\sum_i v_i |\varphi_i(\mathbf{r})|^2 = n(\mathbf{r})$ . This gives

$$\begin{aligned} \left[ -\frac{1}{2}\nabla^2 + v_1(\mathbf{r}) \right] \varphi_i(\mathbf{r}) &= \varepsilon_i \varphi_i(\mathbf{r}) \\ \sum_i v_i |\varphi_i(\mathbf{r})|^2 &= n(\mathbf{r}), \end{aligned} \quad (27)$$

where the potential  $v_1(\mathbf{r})$  is the Lagrange parameter for the density. To fully specify these equations one needs a rule for the occupation  $v_i$  of the orbitals. The Kohn–Sham choice corresponds to occupy the orbitals in the same way as for a Slater determinant. This determinant is the wavefunction of a system of  $N$  non-interacting electrons constrained to have the same one-electron density of the physical system, and leads to the identification

$$T_s[n] = \min_{\{\varphi_i\} \rightarrow n} \sum_i \left\langle \varphi_i \left| -\frac{1}{2}\nabla^2 \right| \varphi_i \right\rangle, \quad (28)$$

with the same  $T_s[n]$  of equation (20). The ground-state energy of the physical system is then obtained via the Hartree-exchange-correlation functional  $E_{\text{Hxc}}[n]$ , defined

as the difference  $F[n; V_{ee}, T] - T_s[n]$ . This also implies that, in equation (27),  $v_1(\mathbf{r}) = v_{\text{KS}}(\mathbf{r}) = v_{\text{nc}}(\mathbf{r}) + \delta E_{\text{Hxc}}[n]/\delta n(\mathbf{r})$ .

Usually, the KS equations are derived starting from the non-interacting system with density  $n(\mathbf{r})$ , rather than from a constrained minimization of  $\sum_i v_i \langle \varphi_i | -\frac{1}{2}\nabla^2 | \varphi_i \rangle$ . This different way of proceeding allows us to keep the analogy with what we will do in the next subsection for APDFT.

### 3.6. APDFT – effective equations

Since the e–e interaction is spherically symmetric, the relevant APD that determines  $\langle \Psi | V_{ee} | \Psi \rangle$  is a unidimensional quantity. To obtain simple ‘two-particle’ equations for  $f(r_{12})$  we start from the kinetic energy operator for the scalar relative coordinate  $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$ ,

$$T_{12} = -\nabla_{r_{12}}^2 = -\frac{1}{r_{12}} \frac{d^2}{dr_{12}^2} r_{12} + \frac{\ell(\ell+1)}{r_{12}^2}, \quad (29)$$

and we perform a minimization of  $\sum_i \vartheta_i \langle \psi_i | -\nabla_{r_{12}}^2 | \psi_i \rangle$  with respect to some orthogonal ‘effective’ geminals  $\psi_i(r_{12})$  constrained to yield  $f$  of the physical system,  $\sum_i \vartheta_i |\psi_i|^2 = f$  leading to

$$\begin{aligned} [-\nabla_{r_{12}}^2 + w_{\text{eff}}(r_{12})] \psi_i(r_{12}) &= \epsilon_i \psi_i(r_{12}) \\ \sum_i \vartheta_i |\psi_i(r_{12})|^2 &= f(r_{12}). \end{aligned} \quad (30)$$

The interaction  $w_{\text{eff}}(r_{12})$  is the Lagrange parameter for  $f$ . Again, to fully specify these equations we need a rule for the occupancy  $\vartheta_i$  of the effective geminals. For spin compensated systems, we can choose to apply a rule that resembles to a Slater determinant: occupancy 1 for even  $\ell$  (single symmetry), occupancy 3 for odd  $\ell$  (triplet symmetry), up to  $N(N-1)/2$  occupied geminals. This rule has been applied to solve the effective equations (30) in the uniform electron gas, with rather accurate results [23–25]. It is, however, important to point out that when we apply this occupancy rule to equations (30)

- (1) There is no Slater determinant that can be associated with our effective geminals: the  $\psi_i$  are constrained to give the *exact*  $f$  that cannot be obtained from a non-interacting wavefunction (for example, any Slater determinant violates the cusp condition satisfied by the exact  $f$ );
- (2) More generally, there is no wavefunction (and so no physical system) that can be built from our effective geminals.

This last point implies that, if we define

$$T_g[f] = \min_{\{\psi_i\} \rightarrow f} \sum_i \langle \psi_i | -\nabla_{r_{12}}^2 | \psi_i \rangle \quad (31)$$

(with the determinant-like occupancy), we have in general

$$T_g[f] \neq T_f[f], \quad (32)$$

where  $T_f[f]$  was defined in equation (25). The total energy of the physical system can then be recovered via the kinetic and external-potential functional defined in reference [5],  $F_{\text{KE}}[f; V_{\text{ne}}] = G[f; V_{\text{ne}}, T] - T_{\text{gl}}[f]$ . This also leads to the identification, in equation (30),  $w_{\text{eff}}(r_{12}) = 1/r_{12} + \delta F_{\text{KE}}[f; V_{\text{ne}}]/\delta f(r_{12})$ .

An important issue to be addressed concerning the effective equations (30) is whether a given physical (and thus  $N$ -representable)  $f(r_{12})$  is also representable by the simple ‘effective-geminal’ decomposition of equations (30). This question is similar to the one arising in DFT: is a physical density always non-interacting representable? In view of the more complex nature of  $f(r_{12})$  with respect to  $n(\mathbf{r})$  we might expect that this problem is much more difficult to face in APDFT than in DFT. It seems reasonable that at least the short-range part of a physical  $f(r_{12})$  is representable by equations (30), while the long-range tail of  $f$  of an extended system could be problematic [26].

#### 4. Simple physical examples: two-electron systems

In this section we give some examples for two-electron systems, in order to gain physical insight with some of the ideas just introduced.

##### 4.1. A picture from harmonic forces

A very simple picture of the whole adiabatic connection path in both DFT and APDFT can be gained by looking at an analytic-solvable model, i.e. a two-electron hamiltonian with only harmonic forces (harmonic electron–nucleus attraction, and harmonic e–e repulsion too) [11],

$$H(K, k) = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{2}K r_1^2 + \frac{1}{2}K r_2^2 - \frac{1}{2}k|\mathbf{r}_1 - \mathbf{r}_2|^2, \quad (33)$$

where  $K > 0$  (attractive nucleus–electron potential),  $k > 0$  (repulsive e–e interaction), and  $K > 2k$ , to have a bound system. For this hamiltonian,

$$n(r) = \frac{2\beta^{3/2}}{\pi^{3/2}} e^{-\beta r^2}, \quad \beta = \frac{2\sqrt{K(K-2k)}}{\sqrt{K-2k} + \sqrt{K}} \quad (34)$$

$$f(r_{12}) = \frac{\gamma^{3/2}}{\pi^{3/2}} e^{-\gamma r_{12}^2}, \quad \gamma = \frac{1}{2}\sqrt{K-2k}. \quad (35)$$

**4.1.1. DFT.** If our ‘physical’ system corresponds to some  $K=K_{\text{ne}}$  and  $k=k_{\text{ee}}$ , and we want to switch off the e–e interaction (by setting, e.g.  $k=\lambda k_{\text{ee}}$ ) while keeping the density fixed, we will simply have to change  $K_{\text{ne}}$  into  $K(\lambda)$  such that  $\beta$  in equation (34) does not change. The function  $K(\lambda)$  is shown in the upper panel of figure 1 for the case  $K_{\text{ne}}=3$ ,  $k_{\text{ee}}=1$ . We see that, as  $\lambda \rightarrow 0$ ,  $K(\lambda)$  decreases, because a smaller attraction is needed to keep the electrons in the density when there is no e–e repulsion. Of course,  $f(r_{12})$  changes with  $\lambda$ , as shown in the lower panel of figure 1: as  $\lambda$  decreases, the ‘on-top’ value  $f^\lambda(r_{12}=0)$  gets larger.



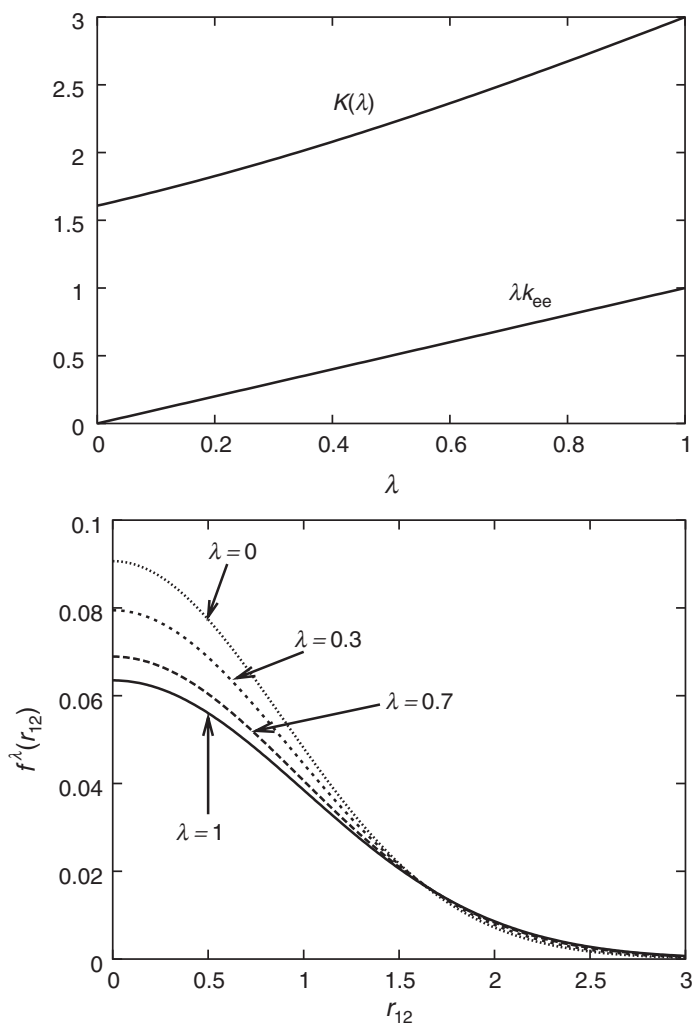


Figure 1. Adiabatic connection in DFT for the simple harmonic hamiltonian of equation (33). The e-e interaction is multiplied by a parameter  $\lambda$ , and the density is kept fixed by a suitable external potential (upper panel). The APD  $f(r_{12})$  changes with  $\lambda$  as shown in the lower panel.

This reflects the fact that when there is no e-e repulsion, it is more likely to find the two electrons close to each other.

**4.1.2. APDFT.** If, instead we switch off the external potential, (e.g. by setting  $K = \xi K_{ne}$ ) while keeping  $f(r_{12})$  fixed, we will have to change the e-e interaction in order to keep  $\gamma$  of equation (35) constant,

$$k(\xi) = \frac{1}{2}(\xi - 1)K_{ne} + k_{ee}. \quad (36)$$

The one-electron density along this adiabatic connection is

$$n^\xi(r) = \frac{2\beta(\xi)^{3/2}}{\pi^{3/2}} e^{-\beta(\xi)r^2}, \quad (37)$$

$$\beta(\xi) = \frac{2\sqrt{\xi K_{ne}(K_{ne} - 2k_{ee})}}{\sqrt{K_{ne} - 2k_{ee} + \sqrt{\xi K_{ne}}}}.$$

Thus  $n^\xi(r)$  is a Gaussian that, as  $\xi \rightarrow 0$ , becomes more and more spread, as shown in the lower panel of figure 2. When the external potential goes to zero, the system

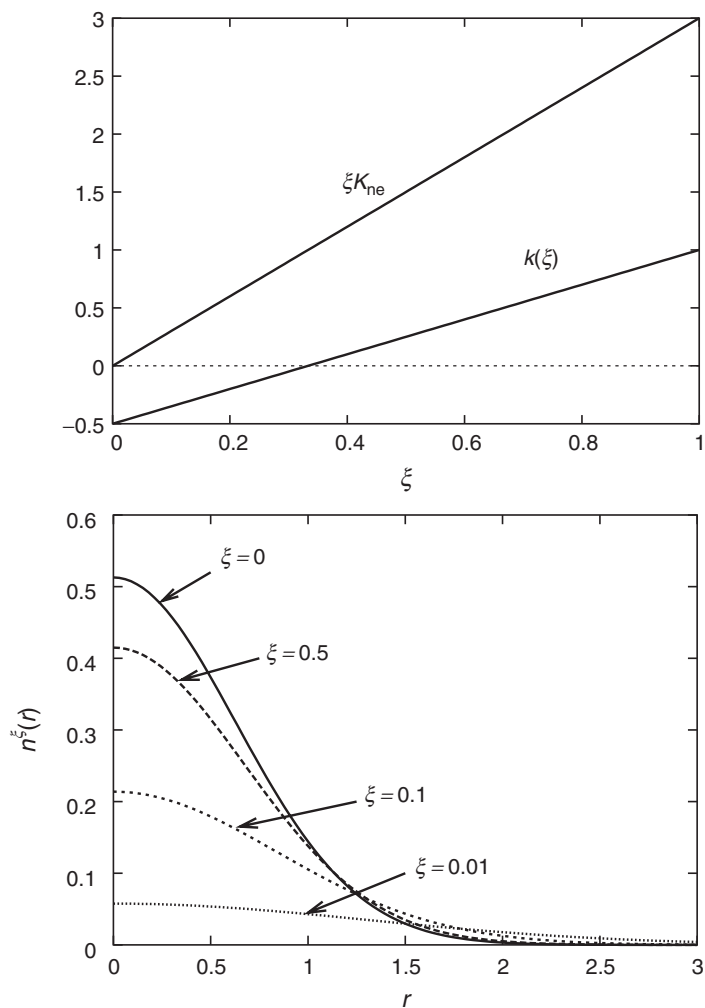


Figure 2. Adiabatic connection in APDFT for the simple harmonic hamiltonian of equation (33). The external potential is multiplied by a parameter  $\xi$ , and the function  $f(r_{12})$  is kept fixed by a suitable e-e interaction (upper panel). The density  $n(r)$  changes with  $\xi$  as shown in the lower panel, and as  $\xi \rightarrow 0$  becomes completely delocalized.

becomes translationally invariant and the wavefunction for the center-of-mass degree of freedom is simply a plane wave. Correspondingly, the e–e interaction changes with equation (36): we see from the upper panel of figure 2 that, as  $\xi$  gets smaller,  $k(\xi)$  becomes smaller (less repulsive), and then it changes sign at some  $0 < \xi < 1$ , becoming an attractive interaction. For a confined system, when the external potential approaches zero, an attractive e–e interaction is needed in order to keep  $f(r_{12})$  fixed. Moreover, in the very special case of harmonic forces there is a value  $\xi^* = 1 - 2k_{ce}/K_{ne} \in (0, 1)$  for which the e–e effective interaction is zero everywhere,  $w^{\xi^*} = 0$ .

Of course, when the e–e physical interaction is the Coulomb potential  $1/r_{12}$  this cannot happen: a system with the same  $f(r_{12})$  of the physical system cannot have  $w=0$  everywhere. This can be simply understood by thinking that there is no external potential that can force the system to have the correct cusp [27] at  $r_{12}=0$ . In fact, along any adiabatic connection that keeps  $f(r_{12})$  fixed, equal to the one of a system with Coulombic e–e interaction,  $w^\xi(r_{12})$  will always behave as  $1/r_{12}$  in the limit of small  $r_{12}$ .

## 4.2. He atom

Consider now the two electrons of a He atom. They feel the attraction of the nucleus,  $-2/r$ , and they repel each other with potential  $1/r_{12}$ . Given the exact (or a very accurate [28]) ground-state wavefunction  $\Psi$ , we can calculate the ‘exact’ density  $n(\mathbf{r})$  and the ‘exact’  $f(r_{12})$ . Now, we can consider the case in which  $W=0$  and  $n(\mathbf{r})$  is kept fixed (the KS system in DFT, section 3.3), and the one in which  $V=0$  and  $f(r_{12})$  is kept fixed (APDFT, section 3.4).

**4.2.1. DFT.** We construct a system which has the same density  $n(\mathbf{r})$  of the physical one and no e–e interaction. This is the KS system, in which the two electrons do not interact ( $w=0$ ) and feel an external potential  $v(r)$  less attractive than  $-2/r$ , as in the case of the harmonic potential of figure 1. The APD  $f^{\lambda=0}(r_{12})$  of this system will be different from the physical one, as shown in figure 3. We see that the change in the function  $f$  when we switch from the physical system to the KS one is qualitatively similar to the one of figure 1, i.e. at  $\lambda=0$  the ‘on-top’ value is higher than the physical one. In the case of Coulomb e–e interaction the physical  $f(r_{12})$  has a cusp,  $f'(0)=f(0)$ , due to the short-range divergence of  $1/r_{12}$  [27].

**4.2.2. APDFT.** In APDFT, we can construct a system which has the same  $f(r_{12})$  of the physical one, and zero external potential ( $V=0$ ). This is a system of two bounded fermions interacting with the effective potential  $w^{\xi=0}(r_{12})$  of figure 4 (calculated from an accurate [5, 28]  $f$ ). As in the case of harmonic forces, the density of this system is completely delocalized, because the wavefunction for the center-of-mass degree of freedom is a plane wave. We can imagine that along the linear adiabatic connection,  $v^\xi(r) = -2\xi/r$ , the corresponding  $w^\xi(r_{12})$  changes smoothly between  $1/r_{12}$  (at  $\xi = \xi_{\text{phys}} = 1$ ) and the potential  $w^{\xi=0}(r_{12})$  of figure 4. As anticipated, we see that at  $\xi=0$  the effective e–e interaction has an attractive part, which is necessary to have the same  $f$  of a physical confined system. However, as already pointed out, for small  $r_{12}$ , the e–e interaction must always behave as  $1/r_{12}$ , to produce the exact cusp in  $f(r_{12})$  [27].

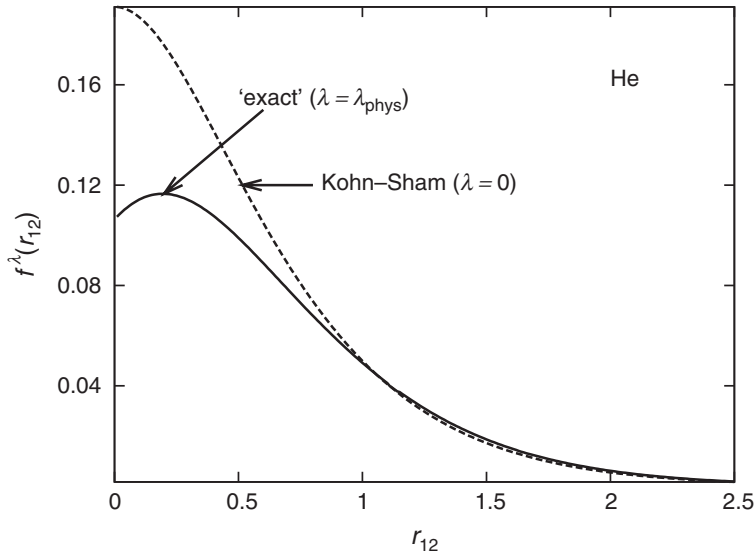


Figure 3. The function  $f^\lambda(r_{12})$  at the two ends of the adiabatic connection in DFT for the He atom. For  $\lambda=0$ , we have a system of two non-interacting ( $W=0$ ) electrons constrained by an external potential to yield the same density of the physical system. For  $\lambda=\lambda_{\text{phys}}$  we have the physical system with full interaction  $1/r_{12}$  and external potential  $-2/r$  (from the wavefunction of [28]; see also [5]).

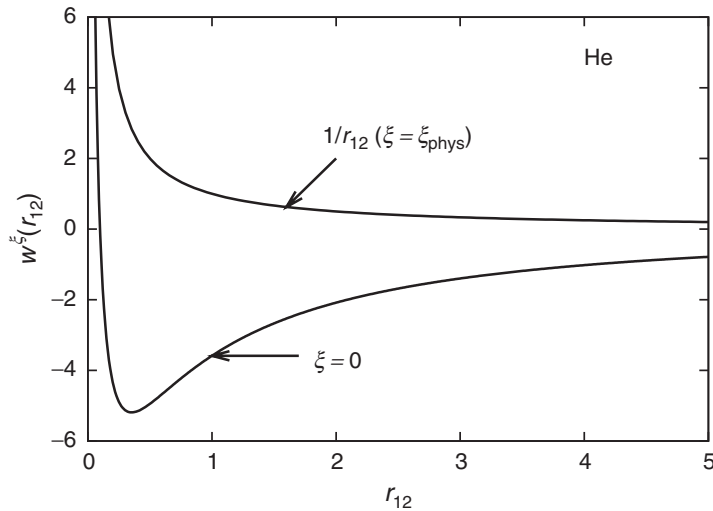


Figure 4. The e-e interaction  $w^\xi(r_{12})$  at the two ends of the adiabatic connection in APDFT for the He atom. For  $\xi=0$  we have a system of two free fermions (zero external potential) interacting with  $w^{\xi=0}(r_{12})$ . This system has the same  $f(r_{12})$  of the physical system, but a completely delocalized one-electron density. For  $\xi=\xi_{\text{phys}}$  we have the physical system, with e-e interaction  $1/r_{12}$  and external potential  $-2/r$ . (The potential  $w$  at  $\xi=0$  has been calculated from the accurate wavefunction of [28]; see [5] for more details.)

## 5. From APDFT to correlation energy functionals for DFT

In section 3 we have underlined the similarity of the roles played by  $n(\mathbf{r})$  and  $f(r_{12})$  from a mathematical point of view: the former completely determines  $\langle \Psi | V_{\text{ne}} | \Psi \rangle$ , and the latter  $\langle \Psi | V_{\text{ee}} | \Psi \rangle$ . However, while the KS system is a substantial simplification of the many-electron problem (yielding to single particle equations), the auxiliary system of section 3.4 (with zero external potential) is still a complicated many-body object, consisting of  $N$  fermions interacting with a partially attractive potential. The radial equations of section 3.6 are a great simplification of the problem, but we might expect that building approximations for the whole functional  $F_{\text{KE}}[f; V_{\text{ne}}]$  could be not easy.

Our basic idea, instead, is to use APDFT to build what is missing in DFT, i.e. to build  $f^\lambda(r_{12})$  along the adiabatic connection in DFT. As said in the Introduction, we insert our approach in the framework of exact-exchange DFT [3, 4, 29, 30] in which only the correlation energy functional needs to be approximated. The ground-state energy of the physical system is given by

$$E_0 = T_s[n] + \int n(\mathbf{r})v_{\text{ne}}(\mathbf{r})d\mathbf{r} + E_{\text{H}}[n] + E_{\text{x}}[n] + E_{\text{c}}[n], \quad (38)$$

where  $E_{\text{H}}[n]$  is the usual Hartree term,  $E_{\text{x}}[n]$  is the exchange energy, obtained by putting the Kohn–Sham orbitals in the Hartree–Fock expression for exchange, and the correlation energy,  $E_{\text{c}}[n]$ , is unknown. Equation (38) can be also rewritten as

$$E_0 = \langle \Phi_{\text{KS}} | T + V_{\text{ee}} + V_{\text{ne}} | \Phi_{\text{KS}} \rangle + E_{\text{c}}[n], \quad (39)$$

where  $\Phi_{\text{KS}}$  is the Slater determinant of KS orbitals, i.e. the wavefunction of  $N$  non-interacting electrons constrained to yield the same  $n(\mathbf{r})$  of the physical system. Combining equation (20) with equation (39), we see that the wanted correlation energy is given by

$$E_{\text{c}}[n] = \int_0^{\lambda_{\text{phys}}} d\lambda \int_0^\infty dr_{12} 4\pi r_{12}^2 f_{\text{c}}^\lambda(r_{12}) \frac{\partial w^\lambda(r_{12})}{\partial \lambda}, \quad (40)$$

where

$$f_{\text{c}}^\lambda(r_{12}) = f^\lambda(r_{12}) - f^{\lambda=0}(r_{12}) = f^\lambda(r_{12}) - f_{\text{KS}}(r_{12}). \quad (41)$$

Thus, in order to get the KS correlation energy, we should compute  $f^\lambda(r_{12})$  for each Hamiltonian  $H^\lambda$  of section 3.3. Our approach consists in solving the simple radial equations of section 3.6 for each  $H^\lambda$  along the adiabatic connection in DFT. This is not particularly expensive: we are dealing with unidimensional equations, and, if the dependence of  $w^\lambda$  on  $\lambda$  is smooth, we will only need few  $\lambda$  values ( $\sim 5\text{--}30$ ) between 0 and  $\lambda_{\text{phys}}$ . With this particular combination of APDFT and DFT, we do not need to approximate the whole functional  $F_{\text{KE}}$  along the DFT adiabatic connection, but only its functional derivative, i.e. the effective interaction  $w_{\text{eff}}(r_{12})$  which appears in equation (30), since the remaining information is provided by DFT. As we

shall see, simple physical arguments can be used to build reasonable approximations for  $w_{\text{eff}}(r_{12})$  at each coupling strength  $\lambda$ .

Since the effective equations yielding  $f_c^\lambda(r_{12})$  must be solved for *each* system, we speak of *system-adapted* correlation energy density functionals.

## 6. Building approximations

In [5], we proposed and successfully tested a simple approximation for building  $w_{\text{eff}}(r_{12})$  along the DFT adiabatic connection for two-electron atoms. This approximation starts from  $w_{\text{eff}}^{(0)}(r_{12})$ , the effective e–e interaction that gives  $f_{\text{KS}}(r_{12})$  when inserted in equations (30). In the special case of two-electron systems,  $w_{\text{eff}}^{(0)}(r_{12})$  is directly available in a KS calculations. For systems with more than two electrons,  $w_{\text{eff}}^{(0)}(r_{12})$  could be calculated, e.g. with the methods in [31, 32]. Then, the idea is to build an approximation for a correlation potential, to be added to  $w_{\text{eff}}^{(0)}(r_{12})$ , which describes the change in  $f$  when the e–e interaction is turned on, from zero to  $w^\lambda(r_{12})$ . To do this, we defined an average density  $\bar{n}$ ,

$$\bar{n} = \frac{1}{N} \int d\mathbf{r} n(\mathbf{r})^2, \quad (42)$$

and, correspondingly, an average radius  $\bar{r}_s$ ,

$$\bar{r}_s = \left( \frac{4\pi\bar{m}}{3} \right)^{-1/3}. \quad (43)$$

We then built a correlation potential  $w_{\text{eff}}^{c,\lambda}(r_{12})$ , as

$$w_{\text{eff}}^{c,\lambda}(r_{12}) = w^\lambda(r_{12}) - \int_{|\mathbf{r}| \leq \bar{r}_s} \bar{n} w^\lambda(|\mathbf{r} - \mathbf{r}_{12}|) d\mathbf{r}. \quad (44)$$

The idea behind equation (44) is the following: the e–e interaction  $w^\lambda$  is screened by a sphere of radius  $\bar{r}_s$  and of positive uniform charge of density  $\bar{n}$  that attracts the electrons with the same interaction  $w^\lambda$ . The average density  $\bar{n}$  of equation (42) (and thus the average  $\bar{r}_s$ ) is kept fixed to mimic the fact that the one-electron density does not change along the adiabatic connection.

In order to gain insight with our construction, let us consider the case of the physical system,  $w^{\lambda=\lambda_{\text{phys}}} = 1/r_{12}$ , for which equation (44) corresponds to

$$w_{\text{eff}}^c(r_{12}) = \left( \frac{1}{r_{12}} + \frac{r_{12}^2}{2\bar{r}_s^3} - \frac{3}{2\bar{r}_s} \right) \theta(\bar{r}_s - r_{12}), \quad (45)$$

where  $\theta(x)$  is the Heaviside step function. Figure 5 shows, for the He atom, the potential  $w_{\text{eff}}^{(0)}$  which generates  $f_{\text{KS}}$ , together with the ‘exact’ correlation potential  $w_{\text{eff}}^c$ , and the approximation of equation (45). We see that the potential  $w_{\text{eff}}^{(0)}$  is a confining potential for the variable  $r_{12}$ : our idea is to include in this term, available from DFT, the contribution to  $f(r_{12})$  coming from the particular external potential

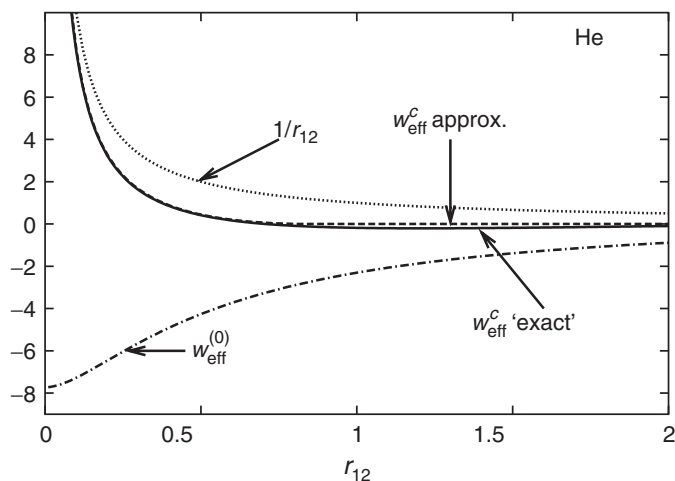


Figure 5. Construction of an approximation for the effective potential that generates the APD  $f(r_{12})$  of the He atom:  $w_{\text{eff}}^{(0)}$  is the part of the potential that generates the APD of the KS system. The ‘exact’ [5, 28] correlation potential  $w_{\text{eff}}^c$  and our approximation of equation (45) are shown, together with the Coulomb repulsion  $1/r_{12}$ .

of the system and from the fermionic structure of the wavefunction. The remaining part to be approximated, the correlation potential  $w_{\text{eff}}^c$ , must include the effect of the e–e repulsion while keeping the density fixed, i.e. it must be essentially a screened Coulomb interaction. We see from figure 5 that the simple approximation of equation (45) is reasonable, i.e. the screening length is well approximated by  $\bar{r}_s$  of equations (42)–(43). For comparison, the full Coulomb repulsion  $1/r_{12}$  is also shown. Notice that in the special case of two-electron systems we have  $T_f[f] = T_f g^{-r}[f]$ , so that the potential  $w^{\xi=0}$  of figure 4 corresponds, in figure 5, to the sum of  $w_{\text{eff}}^{(0)}$  and the ‘exact’  $w_{\text{eff}}^c$ .

In [5], we inserted the potential  $w_{\text{eff}}^{(0)}(r_{12}) + w_{\text{eff}}^{c,\lambda}(r_{12})$  into equations (30), and solved them for several two-electron atoms. Our results can be summarized as follows: (i) at  $\lambda = \lambda_{\text{phys}}$  (i.e. for  $w^\lambda(r_{12}) = 1/r_{12}$ ) we obtained APD  $f(r_{12})$  in close agreement with those coming from accurate variational wavefunctions [28], especially at small  $r_{12}$ ; (ii) by setting  $w^\lambda(r_{12}) = \text{erf}(\lambda r_{12})/r_{12}$  (the ‘erf’ adiabatic connection), the KS correlation energies from equation (40) have an error which is less than 4 mH for nuclear charges  $Z \geq 2$ ; (iii) again with the ‘erf’ adiabatic connection, we found that when the reference system corresponds to some  $\lambda = \mu$  between zero and  $\lambda_{\text{phys}}$  [as in equation (21)] our correlation energies are one order of magnitude better for  $\mu \gtrsim 1/\bar{r}_s$ .

The correlation potential of equation (45), originally proposed by Overhauser [33], has been also used to solve the effective equation (30) for the uniform electron gas (UEG), yielding to a very accurate description of the short-range part of  $f(r_{12})$  at all densities [23]. A more sophisticated effective potential, based on a self-consistent Hartree approximation, extended such accuracy to the long-range part of the UEG  $f(r_{12})$  at metallic densities [24]. Other simple approximations for  $w_{\text{eff}}(r_{12})$  in the UEG have also been proposed and tested [25].

## 7. Conclusions and perspectives

We have presented the ideas concerning a theory based on the spherically and system-averaged pair density  $f(r_{12})$ , and we have suggested to combine it with DFT to obtain system-adapted correlation energy functionals. So far, the method has been tested for the He series [5] and for the uniform electron gas [23–25], yielding promising results.

In order to completely develop the approach presented here, many steps are still to be performed and many issues are to be addressed. Among them, the most relevant ones concern the construction of better approximations for the effective electron–electron interaction that enters the formalism, and the implementation of a self-consistent scheme to combine the Kohn–Sham equations with the correlation energy functional arising from our approach. Last but not least, with the approximations tested so far our approach works very well for the short-range part of  $f(r_{12})$ , so that the combination with multideterminantal DFT [21, 34] (in which only the short-range correlations are treated within DFT) is also very promising and deserves further investigation.

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