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KOHN-SHAM CALCULATIONS COMBINED WITH AN AVERAGE PAIR-DENSITY FUNCTIONAL THEORY

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A recently developed formalism in which Kohn-Sham calculations are combined with an "average pair density functional theory" is reviewed, and some new properties of the effective electron-electron interaction entering in this formalism are derived. A preliminary construction of a fully self-consitent scheme is also presented in this framework.

Keywords: Electronic structure; density functional theory; pair density.

1. Introduction

Kohn-Sham (KS) Density Functional Theory[1–3] (DFT) is nowadays one of the most popular methods for electronic structure calculations both in chemistry and solid-state physics, thanks to its combination of low computational cost and reasonable performances. The accuracy of a KS-DFT result is limited by the approximate nature of the exchange-correlation energy density functional $E_{xc}[n]$. Typical cases in which present-day DFT fails are strongly correlated systems, the description of van der Waals forces, the handling of near degeneracy. Much effort is put nowadays in trying to improve the DFT performances via the construction of better approximations for the KS $E_{xc}[n]$ (for recent reviews, see, e.g., Refs. 2, 3, 4), or via alternative routes, like, e.g., the use of non-KS options.[5] A popular trend in the development of new KS $E_{xc}[n]$ is the use of the exact exchange functional $E_x[n]$ (in terms of the KS orbitals), and thus the search for an approximate, compatible, correlation functional $E_c[n]$.

In this work we review the basis of a theoretical framework[6,7] in which KS-DFT is combined with an "average pair density functional theory" (APDFT) that provides an explicit construction for $E_c[n]$, transfering the work of finding an approximate functional to the search of an effective particle-particle interaction. A self-consitent scheme for this approach is presented, and some new properties of the effective interaction that enters in this combined formalism are derived. Very preliminary applications are discussed.

2. Definitions

Our target problem is finding the ground-state energy of the standard N-electron hamiltonian in the Born-Oppenheimer approximation (in Hartree atomic units, $\hbar = m = a_0 = e = 1$, used throughout),

$$H = T + V_{ee} + V_{ne}, \tag{1}$$

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

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

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

where v_{ne} is the external potential due to nuclei. Given Ψ, the exact 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 electronic density,

$$n(\mathbf{r}) = N \sum_{\sigma_1\ldots\sigma_N} \int |\Psi(\mathbf{r}\sigma_1, \mathbf{r}_2\sigma_2, ..., \mathbf{r}_N\sigma_N)|^2 d\mathbf{r}_2 ... d\mathbf{r}_N, \tag{5}$$

and the spherically and system-averaged pair density $f(r_{12})$ (APD), which is obtained by first considering the pair density $P_2(\mathbf{r}_1, \mathbf{r}_2)$,

$$P_2(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \sum_{\sigma_1\ldots\sigma_N} \int |\Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, \mathbf{r}_3\sigma_3, ..., \mathbf{r}_N\sigma_N)|^2 d\mathbf{r}_3 ... d\mathbf{r}_N, \tag{6}$$

and then by integrating it over all variables except $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$,

$$f(r_{12}) = \frac{1}{2}\int P_2(\mathbf{r}_1, \mathbf{r}_2) \frac{d\Omega_{\mathbf{r}_{12}}}{4\pi} d\mathbf{R}, \tag{7}$$

where $\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$, $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$. The function $f(r_{12})$ is also known in chemistry as intracule density,[8–14] and, in the special case of a an electron liquid of uniform density n, is related to the radial pair-distribution function $g(r_{12})$ by $g(r) = 2f(r)/(nN)$. We thus have

$$\langle\Psi|V_{ne}|\Psi\rangle = \int n(\mathbf{r}) v_{ne}(\mathbf{r}) d\mathbf{r} \tag{8}$$

$$\langle\Psi|V_{ee}|\Psi\rangle = \int \frac{f(r_{12})}{r_{12}} d\mathbf{r}_{12} = \int_0^\infty \frac{f(r_{12})}{r_{12}} 4\pi r_{12}^2 dr_{12}. \tag{9}$$

In the following text we will also deal with modified systems in which the external potential and/or the electron-electron interaction is changed. Thus, the notation V_{ne} and V_{ee} will be used to characterize the physical system, while the modified systems will be defined by $V = \sum_{i=1}^{N} v(\mathbf{r}_i)$ and $W = \frac{1}{2}\sum_{i\neq j}^{N} w(|\mathbf{r}_i - \mathbf{r}_j|)$, where the pairwise interaction w always depends only on $|\mathbf{r}_i - \mathbf{r}_j|$.

3. The Exchange-Correlation Functional of KS-DFT

In standard DFT one defines a universal functional of the one-electron density $n(\mathbf{r})$ as resulting from a constrained search over all the antisymmetric wavefunctions Ψ that yield n[15]

$$\tilde{F}[n; V_{ee}] = \min_{\Psi \to n} \langle \Psi | T + V_{ee} | \Psi \rangle, \tag{10}$$

or, more completely, as a Legendre transform[16]

$$F[n; V_{ee}] = \sup_{v} \left\{ \min_{\Psi} \langle \Psi | T + V_{ee} + V | \Psi \rangle - \int n(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \right\}. \tag{11}$$

In both Eqs. (10) and (11), the dependence on the electron-electron interaction has been explictly shown in the functional. The universality of the functional F stems exactly from the fact that the e-e interaction is always $1/r_{12}$. The ground-state energy E_0 of the system can then be obtained by minimizing the energy with respect to n,

$$E_0 = \min_{n} \left\{ F[n; V_{ee}] + \int n(\mathbf{r}) v_{ne}(\mathbf{r}) d\mathbf{r} \right\}. \tag{12}$$

A possible way to derive the Kohn-Sham equations in DFT is to define a set of hamiltonians depending on a real parameter λ,[17–19]

$$H^{\lambda} = T + W^{\lambda} + V^{\lambda}, \tag{13}$$

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

$$n^{\lambda}(\mathbf{r}) = n(\mathbf{r}) \qquad \forall \lambda. \tag{14}$$

If $W^{\lambda_{\text{phys}}} = V_{ee}$ and $W^{\lambda=0} = 0$ (e.g., $W^{\lambda} = \lambda V_{ee}$), one can slowly switch off the electron-electron interaction, while keeping the density fixed via a suitable external potential V^{λ}. Obviously, the APD $f(r_{12})$ changes with λ. By the Hellmann-Feynmann theorem,

$$\frac{\partial E_0^{\lambda}}{\partial \lambda} = \langle \Psi^{\lambda} | \frac{\partial W^{\lambda}}{\partial \lambda} + \frac{\partial V^{\lambda}}{\partial \lambda} | \Psi^{\lambda} \rangle = \int f^{\lambda}(r_{12}) \frac{\partial w^{\lambda}(r_{12})}{\partial \lambda} d\mathbf{r}_{12} + \int n(\mathbf{r}) \frac{\partial v^{\lambda}(\mathbf{r})}{\partial \lambda} d\mathbf{r}, \tag{15}$$

so that by directly integrating Eq. (15), and by combining it with Eq. (12), one obtains

$$F[n; V_{ee}] = T_s[n] + \int_0^{\lambda_{\text{phys}}} d\lambda \int d\mathbf{r}_{12} f^{\lambda}(r_{12}) \frac{\partial w^{\lambda}(r_{12})}{\partial \lambda}, \tag{16}$$

where $T_s[n] = F[n; 0]$ is the kinetic energy of a noninteracting system of N spin-$\frac{1}{2}$ fermions with density $n(\mathbf{r})$. The adiabatic connection in DFT thus naturally defines the Kohn-Sham non-interacting kinetic energy functional $T_s[n]$. The second term in the right-hand-side of Eq. (16) is an exact expression, in terms of the APD $f^{\lambda}(r_{12})$, for the Hartree and the exchange-correlation functional, $E_H[n] + E_{xc}[n]$. The one-body potential at $\lambda = 0$ is the familiar Kohn-Sham potential, $v^{\lambda=0}(\mathbf{r}) = v_{\text{KS}}(\mathbf{r})$.

The traditional approach of DFT to construct approximations for $E_{xc}[n]$ is based on the idea of universality. For example, the familiar local-density approximation (LDA) consists in transfering, in each point of space, the pair density from the uniform electron gas to obtain an approximation for $f^{\lambda}(r_{12})$ in Eq. (16). Our aim is to develop an alternative strategy in which realistic APD $f^{\lambda}(r_{12})$ along the DFT adiabatic connection are constructed via a formally exact theory that must be combined with the KS equations in a self-consitent way. The formal justification for this "average pair-density functional theory" (APDFT) is the object of the next Sec. 4.

4. Average Pair Density Functional Theory

As shown by Eqs. (8) and (9), the APD $f(r_{12})$ couples to the operator V_{ee} in the same way as the electronic density $n(\mathbf{r})$ couples to V_{ne}. In order to derive an "average pair density functional theory" (APDFT) we thus simply repeat the steps of the previous Sec. 3 by switching the roles of f and n, and of V_{ee} and V_{ne}.[7]

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

$$\tilde{G}[f; V_{ne}] = \min_{\Psi \to f} \langle \Psi | T + V_{ne} | \Psi \rangle, \tag{17}$$

where, again the minimum is over all antisymmetric wavefunction Ψ that yield a given $f(r_{12})$. We can also define the system-dependent functional G as

$$G[f; V_{ne}] = \sup_{w} \left\{ \min_{\Psi} \langle \Psi | T + W + V_{ne} | \Psi \rangle - \int f(r_{12}) w(r_{12}) d\mathbf{r}_{12} \right\}. \tag{18}$$

The ground-state energy could then be obtained as

$$E_0 = \min_{f \in \mathcal{N}_f} \left\{ G[f; V_{ne}] + \int \frac{f(r_{12})}{r_{12}} d\mathbf{r}_{12} \right\}, \tag{19}$$

where $\mathcal{N}_f$ is the space of all N-representable APD (i.e., coming from the contraction of an N-particle antisymmetric wavefunction). The definition of the space $\mathcal{N}_f$ is evidently related to the N-representability conditions for the pair density, for which recent interesting progresses have been made.[20] In our case, however, we combine APDFT with DFT so that the minimization of Eq. (19) is never directly carried on.

In order to find the analog of the KS system for APDFT, we define an adiabatic connection similar to the one of Eq. (13) in which, this time, we switch off the external potential. We thus introduce a set of hamiltonians depending on a real parameter ξ,

$$H^{\xi} = T + W^{\xi} + V^{\xi}, \tag{20}$$

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

$$f^{\xi}(r_{12}) = f(r_{12}) \qquad \forall \xi. \tag{21}$$

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

$$\frac{\partial E_0^{\xi}}{\partial \xi} = \langle \Psi^{\xi} | \frac{\partial W^{\xi}}{\partial \xi} + \frac{\partial V^{\xi}}{\partial \xi} | \Psi^{\xi} \rangle = \int f(r_{12}) \frac{\partial w^{\xi}(r_{12})}{\partial \xi} d\mathbf{r}_{12} + \int n^{\xi}(\mathbf{r}) \frac{\partial v^{\xi}(\mathbf{r})}{\partial \xi} d\mathbf{r}, \quad (22)$$

so that

$$G[f; V_{ne}] = T_{\rm f}[f] + \int_0^{\xi_{\rm phys}} d\xi \int d\mathbf{r}\, n^{\xi}(\mathbf{r}) \frac{\partial v^{\xi}(\mathbf{r})}{\partial \xi}, \quad (23)$$

where $T_{\rm f}[f]$ is the kinetic energy of a system of N free (zero external potential) interacting spin-$\frac{1}{2}$ fermions having the same $f(r_{12})$ of the physical system. In the case of a confined system (atoms, molecules) the effective interaction $w^{\xi=0}(r_{12})$ must have an attractive tail: the hamiltonian corresponding to $\xi = 0$ in Eq. (20) describes a cluster of fermions whose center of mass is translationally invariant. The functional $T_{\rm f}[f]$ is the internal kinetic energy of this cluster.

To fix the ideas, consider the simple case of two electrons, e.g. the He atom. When $\xi = 0$, we have two fermions in a relative bound state (similar to the case of positronium, but with a different interaction). This relative bound state is such that the square of the wavefunction for the relative coordinate r_{12} is equal to $f(r_{12})$ of the starting physical system. The corresponding effective interaction $w^{\xi=0}(r_{12})$, obtained[7] by inversion from a very accurate wavefunction,[21] is shown in Fig. 1, for the case of the He atom.

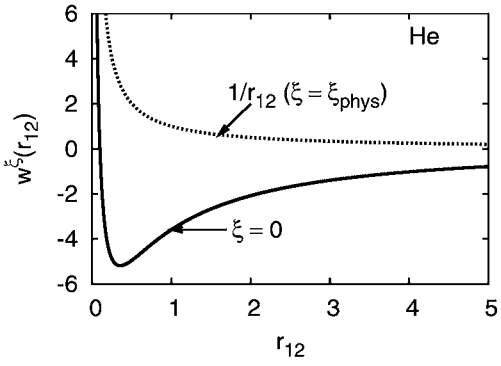

Fig. 1. The electron-electron interaction at the two ends of the APDFT adiabatic connection of Eqs. (20)-(21) in the case of the He atom.

For more than two electrons, $T_{\rm f}[f]$ is still a complicated many-body object. Moreover, since the corresponding $w^{\xi=0}(r_{12})$ can have an attractive tail (as in the case

$N = 2$), we may have an "exotic" true ground-state for the cluster, i.e., the cluster state with the same $f(r_{12})$ of the physical system can be an excited state. However, we have to keep in mind that our aim is not to solve the many-electron problem by means of APDFT alone: we want to use APDFT to produce realistic $f(r_{12})$ along the DFT adiabatic connection of Eqs. (13)-(14). To this end, we proposed[6,7] an approximation for the functional $T_{\rm f}[f]$ based on a geminal decomposition,

$$T_g[f] = \min_{\{\psi_i\}\to f} \sum_i \vartheta_i \langle \psi_i | - \nabla^2_{r_{12}} | \psi_i \rangle, \tag{24}$$

where $\psi_i(r_{12})$ are some effective geminals (orbitals for two electrons, but only depending on the relative distance r_{12}), and ϑ_i some occupancy numbers to be chosen. For example, one can always make a "bosonic" choice, by occupying only one geminal,[22] equal to $\sqrt{f(r_{12})}$. The geminals $\psi_i(r_{12})$ then satisfy the equations

$$\begin{cases} [-\nabla^2_{r_{12}} + w_{\rm eff}(r_{12})]\psi_i(r_{12}) = \epsilon_i \psi_i(r_{12}) \\ \sum_i \vartheta_i |\psi_i(r_{12})|^2 = f(r_{12}), \end{cases} \tag{25}$$

with

$$w_{\rm eff}(r_{12}) = \frac{1}{r_{12}} + \frac{\delta G[f]}{\delta f(r_{12})} - \frac{\delta T_g[f]}{\delta f(r_{12})}. \tag{26}$$

The approximation of Eq. (24) is mainly motivated by the need of having simple equations for $f(r_{12})$ (the one-dimensional character of Eqs. (25) is of course very appealing). Notice that only in the case $N = 2$ we have $T_g[f] = T_{\rm f}[f]$, and thus the effective interaction $w_{\rm eff}(r_{12})$ of Eqs. (25) becomes equal to $w^{\xi=0}(r_{12})$.

5. Combining DFT and APDFT in a Self-Consistent Way

As explained in the previous sections, to compute the expectation value of the physical hamiltonian of Eq. (1) we only need $f(r_{12})$ and $n(\mathbf{r})$ for V_{ee} and V_{ne}, and the non-interacting KS kinetic energy $T_s[n]$ plus the APD $f^\lambda(r_{12})$ along the DFT adiabatic connection (13) for the expectation value of T; schematically:

$$\langle \Psi | H | \Psi \rangle = \underbrace{\langle \Psi | T | \Psi \rangle}_{T_s[n]+f^\lambda(r_{12})} + \underbrace{\langle \Psi | V_{ee} | \Psi \rangle}_{f(r_{12})} + \underbrace{\langle \Psi | V_{ne} | \Psi \rangle}_{n(\mathbf{r})}. \tag{27}$$

Our aim is to obtain $n(\mathbf{r})$ and $T_s[n]$ via the KS equations, and $f^\lambda(r_{12})$ via Eqs. (25), which can be generalized to any hamiltonian along the DFT adiabatic connection, by simply replacing the physical hamiltonian H with H^λ of Eqs. (13)-(14) in the steps of Sec. 4.

A self-consitent scheme for this construction reads

$$(T + V_{\rm KS})\,\Phi_{\rm KS} = E_{\rm KS}\Phi_{\rm KS} \qquad \Rightarrow \qquad n(\mathbf{r}),\ T_s[n] \tag{28}$$

$$\begin{cases} [-\nabla^2_{r_{12}} + w^\lambda_{\rm eff}(r_{12};[n])]\psi^\lambda_i(r_{12}) = \epsilon^\lambda_i \psi^\lambda_i(r_{12}) \\ \sum_i \vartheta_i |\psi^\lambda_i(r_{12})|^2 = f^\lambda(r_{12}), \end{cases} \qquad \Rightarrow \qquad f^\lambda(r_{12}) \tag{29}$$

$$E_0 = \min_{v_{\rm KS}} \left\{ T_s[n] + \int_0^{\lambda_{\rm phys}} d\lambda \int d\mathbf{r}_{12} f^\lambda(r_{12}) \frac{\partial w^\lambda(r_{12})}{\partial \lambda} + \int d\mathbf{r}\, n(\mathbf{r}) v_{ne}(\mathbf{r}) \right\}. \tag{30}$$

The computation starts with a trial $v_{\rm KS}(\mathbf{r})$ in the KS equations, schematically represented by Eq. (28), where $\Phi_{\rm KS}$ is the Slater determinant of KS orbitals. From the KS equations we thus get a first approximation for the density $n(\mathbf{r})$ and the non-interacting kinetic energy $T_s[n]$. Provided that we have a prescription to build an approximate $w^{\lambda}_{\rm eff}$ for a given density $n(\mathbf{r})$ (see next Sec. 6), we can obtain $f^{\lambda}(r_{12})$ along the DFT adiabatic connection from Eqs. (29). In general, this step is not expensive: Eqs. (29) are unidimensional, and if the dependence of $w^{\lambda}(r_{12})$ on λ is smooth, few λ values (5-20) are enough to provide a good estimate of the coupling-constant average. The physical ground-state energy E_0 is then evaluated via Eq. (30). The procedure should then be repeated by optimizing the KS potential $v_{\rm KS}$, so that E_0 is minimum. The N-representability problem of the KS exchange-correlation functional is clearly shifted to the N-representability problem for $f^{\lambda}(r_{12})$. In view of the new conditions derived for the pair density,[20] this seems to leave space for improvements.

6. Properties of the Effective Electron-Electron Interaction

So far, we have only replaced the problem of finding an approximation for $E_{xc}[n]$ with the problem of constructing $w^{\lambda}_{\rm eff}(r_{12};[n])$. In order to proceed further, we study here the properties of $w^{\lambda}_{\rm eff}(r_{12};[n])$.

If we want our Eqs. (28)-(30) to be fully self-consitent, we should impose that for $\lambda = 0$ Eqs. (29) yield $f^{\lambda=0}(r_{12}) = f_{\rm KS}(r_{12})$, i.e., the same APD we would obtain by inserting the KS Slater determinant of Eq. (28) in Eqs. (6)-(7). This corresponds, in the usual DFT language, to treat exchange exactly. The first property we should thus impose to $w^{\lambda}_{\rm eff}(r_{12})$ is

$$w^{\lambda=0}_{\rm eff}(r_{12}) = w^{\rm KS}_{\rm eff}(r_{12}). \tag{31}$$

If we use only one geminal to define $T_g[f]$ in Eq. (24), the property (31) corresponds to $w^{\lambda=0}_{\rm eff}(r_{12}) = \nabla^2\sqrt{f_{\rm KS}(r_{12})}/\sqrt{f_{\rm KS}(r_{12})}$. For more than one geminal we need more sophisticated constructions, mathematically equivalent to those used to construct the KS potential $v_{\rm KS}(r)$ for a given spherical density $n(r)$.[23] Equation (31) also provides a very good starting point to build $w^{\lambda}_{\rm eff}(r_{12})$: the KS system already takes into account the fermionic structure and part of the effect of the external potential in the physical problem. What is then left, that needs to be approximated, is the effect of turning on the electron-electron interaction without changing the one-electron density $n(\mathbf{r})$, and the difference between $T_{\rm f}[f]$ and $T_g[f]$.

For confined systems (atoms, molecules) another property to be imposed on $w^{\lambda}_{\rm eff}(r_{12})$ concerns the eigenvalue $\epsilon^{\lambda}_{\rm max}$ corresponding to the highest occupied geminal in Eqs. (29). In fact, the asymptotic behavior of the pair density $P_2(\mathbf{r}_1,\mathbf{r}_2)$ of Eq. (6) for $|\mathbf{r}_1| \to \infty$ (or $|\mathbf{r}_2| \to \infty$) is, in this case,[24]

$$\lim_{|\mathbf{r}_1|\to\infty} P_2(\mathbf{r}_1,\mathbf{r}_2) = n(\mathbf{r}_1)n_{N-1}(\mathbf{r}_2)\{\hat{\mathbf{r}}_1\}, \tag{32}$$

where $n_{N-1}(\mathbf{r})$ is one of the degenerate ground-state densities of the $(N-1)$-electron system (in the same external potential V_{ne}), with the choice depending

parametrically upon the direction $\hat{\mathbf{r}}_1 = \mathbf{r}_1/|\mathbf{r}_1|$. A similar expansion holds for the KS pair density, obtained from the KS Slater determinant of Eq. (28),

$$\lim_{|\mathbf{r}_1|\to\infty} P_2^{\rm KS}(\mathbf{r}_1,\mathbf{r}_2) = n(\mathbf{r}_1) n_{N-1}^{\rm KS}(\mathbf{r}_2)\{\hat{\mathbf{r}}_1\}, \tag{33}$$

where we have used the fact that, by construction, the N-electron density is the same for the physical system and for the KS one (while, of course, the corresponding $(N-1)$-electron densities are in general different). For a given attractive (atomic, molecular) external potential vanishing at large distances, the N-electron density is in general more diffuse (decaying slower at large distances) than the $(N-1)$-electron density, so that the asymptotic behavior of the APD $f(r_{12})$ is, for large r_{12}, dominated by the N-electron density decay at large distances. We thus see, from Eqs. (32) and (33), that the corresponding APD's, $f(r_{12})$ and $f_{\rm KS}(r_{12})$, will have the same large-r_{12} decay, $\propto e^{\sqrt{-2\epsilon_{\rm max}}\, r_{12}}$, with a different prefactor (which can also include a polynomial function of r_{12}), depending on the difference between $n_{N-1}(\mathbf{r})$ and $n_{N-1}^{\rm KS}(\mathbf{r})$. Since the same expansion holds for any $P_2^\lambda(\mathbf{r}_1,\mathbf{r}_2)$ along the DFT adiabatic connection,

$$\lim_{|\mathbf{r}_1|\to\infty} P_2^\lambda(\mathbf{r}_1,\mathbf{r}_2) = n(\mathbf{r}_1) n_{N-1}^\lambda(\mathbf{r}_2)\{\hat{\mathbf{r}}_1\}, \tag{34}$$

the highest eigenvalue $\epsilon_{\rm max}^\lambda$ in Eqs. (29) must be independent of λ and equal to the one for the KS APD,

$$\epsilon_{\rm max}^\lambda = \epsilon_{\rm max}^{\lambda=0} = \epsilon_{\rm max}^{\rm KS}. \tag{35}$$

In particular, if we choose only one geminal[22] for the definition of $T_g[f]$, there is only one eigenvalue, which must be the same for every λ.

For an extended system we have scattering states in Eqs. (29). For the special case of the uniform electron gas, Eqs. (29) become equivalent to an approach that was first proposed by Overhauser,[25] and further developed by other authors in the past five years.[26–28] In this approach, the geminal occupancy numbers ϑ_i are the same as the ones for a Slater determinant: occupancy 1 for singlet states (even relative angular momentum ℓ), and occupancy 3 for triplet states (odd relative angular momentum ℓ), up to $N(N-1)/2$ geminals. Rather simple approximations for the effective potential $w_{\rm eff}^\lambda(r_{12})$ gave good results[26–28] for the radial distribution function $g(r_{12})$, when compared with quantum Monte Carlo data. The long-range asymptotic behavior, in this case, corresponds to a phase-shift sum rule for the interaction $w_{\rm eff}^\lambda(r_{12})$.[29] The choice of one geminal for the uniform electron gas has been explored, with remarkable success, in Ref. 30. In this case, the formal similarity with the Fermi-hypernetted-chain approach[31] (FHCN) was exploited to build a good approximation for $w_{\rm eff}^\lambda(r_{12})$ (which was split into $\uparrow\uparrow$ and $\uparrow\downarrow$ contributions).

Finally, the small-r_{12} behavior of the effective potential $w_{\rm eff}^\lambda(r_{12})$ is determined by the choice of the adiabatic connection path. For instance, if we choose $w^\lambda(r_{12}) = \lambda/r_{12}$ in Eqs. (13)-(16), then the APD $f^\lambda(r_{12})$ displays the electron-electron cusp $f^\lambda(r_{12}\to 0) = f^\lambda(0)(1+\lambda\, r_{12} + ...)$, which implies, in turn, that also $w_{\rm eff}^\lambda$ must

behave, *for small* r_{12}, as $w_{\rm eff}^{\lambda}(r_{12} \to 0) = \lambda/r_{12} + ...$ In particular, for $\lambda = \lambda_{\rm phys}$, we always have $w_{\rm eff}^{\lambda_{\rm phys}}(r_{12} \to 0) = 1/r_{12} + ...$, as shown, for the case of the He atom in Fig. 1. If we choose a cuspless nonlinear path, like $w^{\lambda}(r_{12}) = {\rm erf}(\lambda r_{12})/r_{12}$, then the small r_{12} behavior of $w_{\rm eff}^{\lambda}(r_{12})$ is known only when we are approaching the physical interaction.[32]

7. Preliminary Applications

The construction of an approximate $w_{\rm eff}^{\lambda}(r_{12};[n])$ can thus start with the decomposition

$$w_{\rm eff}^{\lambda}(r_{12};[n]) = w_{\rm eff}^{\rm KS}(r_{12}) + w^{\lambda}(r_{12}) + \Delta w_{\rm eff}^{\lambda}(r_{12};[n]), \tag{36}$$

where the term $\Delta w_{\rm eff}^{\lambda}(r_{12};[n])$ should take care of the fact that, when the electron-electron interaction is turned on, the one-electron density $n(\mathbf{r})$ and (for confined systems) the highest eigenvalue $\epsilon_{\rm max}^{\lambda}$ do not change.

As a starting point, we applied the method of Eqs. (28)-(30) to the He isoelectronic series. In this simple (yet not trivial) 2-electron case, we have the advantage that we can treat $T_{\rm f}[f]$ exactly. We developed an approximation[6] for $\Delta w_{\rm eff}^{\lambda}(r_{12};[n])$ based on the one used for the uniform electron gas.[26] This approximation is designed to mimic the conservation of $n(\mathbf{r})$ along the DFT adiabatic connection, but does not take into account the eigenvalue conservation. It works remarkably well when combined with a nonlinear adiabatic connection path $w^{\lambda}(r_{12}) = {\rm erf}(\lambda r_{12})/r_{12}$ that separates short- and long-range correlation effects, and is reported in the Appendix of Ref. 6. Preliminary implementations of the self-consitent procedure of Eqs. (28)-(30) yield ground-state energies within 1 mH with respect to full configuration interaction (CI) calculations in the same basis set. However, the way we carried out these first tests was simply based on a direct minimization of few variables parametrizing $v_{\rm KS}(\mathbf{r})$. This rather inefficient way to implement Eqs. (28)-(30) needs further improvment. Besides, the Kohn-Sham potentials we obtain in this way are very unstable (like the ones of Ref. 33), although the corresponding total energies and electronic densities are stable, and do not display the variational collapse of perturbation-theory-based approximate $E_c[n]$.[34]

8. Perspectives

The generalization to many-electron systems of nonuniform density of the approximation built in Ref. 6 for $w_{\rm eff}^{\lambda}(r_{12})$ is not straightforward. If we simply apply it to the Be atom case (by using only one geminal), we obtain energy errors of 300 mH. Adding the eigenvalue conservation can improve the results, but, of course, there is not a unique way to impose it. So far, we found that the final outcome strongly depends on how we impose the eigenvalue conservation (i.e., if we use a functional form with one parameter adjusted to keep the eigenvalue independent of λ, the results drastically depend on the chosen functional form). It seems thus necessary to switch to more than one geminal, and/or to find better constructions for $w_{\rm eff}^{\lambda}(r_{12})$.

In particular, it may be promising to explore the possibility to construct approximations inspired to the FHNC,[30,31,35] and to try to include some of the new results on N-representability conditions for the pair density.[20] Different approximations with respect to the one of Eq. (24) for the functional $T_{\rm f}[f]$, and the use of Eq. (23) also deserve further investigation.

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