

Some questions on the exchange contribution to the effective potential of the Kohn–Sham theory

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Abstract The current success of Density Functional Theory applications hinges upon the availability of explicitly density-dependent functionals to self-consistently solve a set of one-electron equations, the Kohn–Sham (KS) equations, which determine the occupied orbitals and its associated electronic density. In KS theory, a local exchange potential is proposed as part of an effective potential. This potential is compared to the exchange operator of the Hartree–Fock theory, which is of a non-local nature. The present paper discusses the variational framework of the KS equations, and the equivalence between both exchange potentials within a correlation-free theory. The common difficulties of current local exchange functionals to correctly simulate the non-locality of the exchange energy density in chemical systems are also analyzed and explained through an exactly solvable model. We give then numerical arguments and conclude by analyzing the performance of various commonly used approximations to exchange functionals.

1 Introduction

The Kohn–Sham (KS) theory [1, 2] is probably today the most accepted and widely used computational tool for applications to atoms, molecules, mesoscopic and

extended systems. Needless to say, this theory is widely considered a powerful and reliable alternative to other quantum chemical methods rooted on approximations to the exact electronic wave function. The way in which the KS equations are solved, having a relatively low computational cost compared with traditional *ab initio* methods, has profoundly impacted in last years the field of quantum chemistry. Additionally, the myriad of applications to problems of the highest chemical interest has led to a deep knowledge of its accuracy with respect to the most employed approximations; however, despite its successful application to almost all domains of computational chemistry and physics, we still miss a more rigorous, systematic and widely enough analysis on some fundamental aspects of the theory. Particularly, the traversing connection between KS equations and variational theories might still need further work in order to shed light about the discussion recently opened in the literature [3–13]. Note that we aim at further discussing the implications of one of the key points of the KS theory; i.e., the local nature of the effective potential, which is implicitly at the core of the theory and manifests itself in how the equations are assigned to a variational problem. Note also that we do not use the term local as synonymous of local spin density, as historically done though recently disapproved. The outline of the paper is the following. The variational scheme to which the KS equations are related is discussed in detail in Sect. 2. Section 3 is devoted to discuss the implications of the locality hypothesis of the KS potential to obtain the exact solution of the corresponding ground state of the associated interacting systems. Finally, Sect. 4 illustrates the pitfalls of the majority of the exchange potentials commonly found in the literature and how they probably arise from a common origin.

The authors wish to dedicate this work to the memory of Professor Oriano Salvetti, a clever scientist and an excellent teacher.

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2 The Kohn–Sham equations

2.1 Background and previous considerations

We will first establish a few previous definitions by considering the ground state of a N -electron system under the influence of an external potential; it is also assumed here, to keep the discussion as simple as possible, that such ground state is non-degenerate. The energy of such state is written as:

$$E = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle, \quad (1)$$

where the minimization is done among all the well-behaved wave functions satisfying the usual normalization condition ($\int \Psi^* \Psi d\tau = 1$). The Hamiltonian of this systems is (in a.u.):

$$\hat{H} = \hat{T} + \hat{U} + \hat{V}, \quad (2)$$

with

$$\hat{T} = \sum_i^N \left[-\frac{1}{2} \nabla^2(\mathbf{r}_i) \right], \quad (3)$$

$$\hat{U} = \sum_{i < j}^N |\mathbf{r}_i - \mathbf{r}_j|^{-1}, \quad (4)$$

$$\hat{V} = \sum_i^N v(\mathbf{r}_i), \quad (5)$$

being the kinetic energy, the electron repulsion and the external attraction operators, respectively. The Hohenberg–Kohn theorem [1] allows us to rewrite Eq. 1 in an alternative way:

$$E[\rho] = F[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}, \quad (6)$$

where $\rho(\mathbf{r})$ is the exact density of the ground state and $F[\rho]$ is the universal density functional, whose expression can be defined through the constrained search procedure [14]:

$$F[\rho] = \min_{\bar{\rho}(\mathbf{r})} \min_{\Psi \rightarrow \bar{\rho}(\mathbf{r})} \langle \Psi | \hat{T} + \hat{U} | \Psi \rangle, \quad (7)$$

being $\bar{\rho}(\mathbf{r})$ the set of well-behaved densities satisfying now the corresponding normalization condition, $\int \bar{\rho}(\mathbf{r})d\mathbf{r} = N$ (N -representable densities).

The Kohn–Sham theory, as normally formulated, is based on the following major premise: the exact density of the ground state of the interacting N -electron system can be obtained from a non-interacting N -electron system under the influence of an effective local (multiplicative) potential (ω_{eff}). Thus, the wave function of the non-interacting system can be described by a Slater determinant whose spinorbitals are known to be the solution of the following eigenvalue equations, the so-called KS equations:

$$\left[-\frac{1}{2} \nabla^2 + \omega_{\text{eff}} \right] \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}), \quad \forall i \in N. \quad (8)$$

Note that the corresponding KS eigenfunctions always obey the canonical form given by Eq. 8; thus, the orthogonality of these spinorbitals is guaranteed in this way. Finally, the exact density of the interacting ground state might be unambiguously expressed as:

$$\rho(\mathbf{r}) = \sum_i^N \rho_i(\mathbf{r}) = \sum_i^N \varphi_i^*(\mathbf{r})\varphi_i(\mathbf{r}). \quad (9)$$

2.2 The constrained variation of the energy

After this brief introduction, we ask at this stage the following questions: (a) to what extent the hypothesis of locality introduced in the KS theory is strictly needed? and (b) to which variational problem are the set of KS equations linked? In fact, up to two different frameworks are presented in the original work [2]. The first one is a Hartree-like approximation (see Section II.A of [2]), where ω_{eff} is approximated by a local function, whereas the second approach (Section II.B) uses a Hartree–Fock like potential, which is a non-local exchange contribution but built in this case with the spinorbitals arising from the solution of the KS equations. We also remind here that the main hypothesis of the KS theory is perfectly summarized in the “Note added in proof”, which claims that “it is possible, formally, to replace the many-electron problem by an exactly equivalent set of self-consistent one-electron equations... the approximate theory of Sect. 2” if $F[\rho]$ is used in the energy variational principle.

We tackle these issues next by applying the condition of being an extremum to the energy given by Eq. 6, subject to the normalization condition $\int \delta\rho(\mathbf{r})d\mathbf{r} = 0$, which immediately leads to the Thomas–Fermi (TF) like equations:

$$\frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} - v(\mathbf{r}) = \mu, \quad (10)$$

with μ being the Lagrange multiplier needed to introduce the referred normalization condition. The parameter μ lacks a physical meaning except for the case where the energy of Eq. 6 is the free energy corresponding to an ensemble; in that case μ represents the chemical potential of Thermodynamics. Following [1], the universal functional $F[\rho]$ is written as:

$$F[\rho] = T_s[\rho] + \frac{1}{2} \int \rho(\mathbf{r})v_H(\mathbf{r})d\mathbf{r} + E_{xc}[\rho], \quad (11)$$

with the Hartree potential given by:

$$v_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (12)$$

and where $E_{xc}[\rho]$ is the exchange-correlation energy functional needed to guarantee the equality between Eqs. 6 and 11. $T_s[\rho]$ is the kinetic energy of a non-interacting system:

$$T_s[\rho] = \sum_i^N \int \varphi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \varphi_i(\mathbf{r}) \mathbf{d}\mathbf{r}, \quad (13)$$

which, by virtue of the Hohenberg–Kohn (HK) theorem, must be a functional of the charge density because the wavefunction, and hence the spinorbitals, must be also functionals of the density. Therefore, $T_s[\rho]$ is defined to be the ground-state kinetic energy of a non-interacting system whose Hamiltonian operator is:

$$\hat{H}_s = -\frac{1}{2} \sum_i^N \nabla_i^2 + \sum_i^N \omega_{\text{eff}}(\mathbf{r}_i), \quad (14)$$

and for which the energy is $E_s = \sum_i^N \epsilon_i$. According to the HK theorem, the universal functional $F[\rho]$ for the non-interacting system is $T_s[\rho]$ and the ground-state energy could then be written as:

$$E_s[\rho] = T_s[\rho] + \int \rho(\mathbf{r}) \omega_{\text{eff}}(\mathbf{r}) \mathbf{d}\mathbf{r}, \quad (15)$$

whose minimum-energy character can be expressed by applying Levy's constrained search as:

$$\begin{aligned} T_s[\rho] &= \min_{\Phi \rightarrow \rho(\mathbf{r})} \left\langle \Phi \left| -\frac{1}{2} \sum_i^N \nabla_i^2 \right| \Phi \right\rangle \\ &= \min_{\{\varphi\} \rightarrow \rho(\mathbf{r})} \sum_i^N \int \varphi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \varphi_i(\mathbf{r}) \mathbf{d}\mathbf{r}, \end{aligned} \quad (16)$$

with $\rho(\mathbf{r})$ being a reference charge density that, in KS theory, coincides with the ground state charge density of the interacting system. The condition of extremum, $\delta E_s[\rho] = 0$, under the constraint of $\int \delta \rho(\mathbf{r}) \mathbf{d}\mathbf{r} = 0$, leads again to a Thomas–Fermi like equation:

$$\frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} - \omega_{\text{eff}}(\mathbf{r}) = \mu, \quad (17)$$

from which the KS equations cannot be obtained because: (a) they include a single Lagrange multiplier, and (b) the presence of the functional derivative $\delta T_s[\rho]/\delta \rho$. They cannot be obtained by replacing the constraint $\int \delta \rho(\mathbf{r}) \mathbf{d}\mathbf{r} = 0$ by the N normalization conditions:

$$\int \delta \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}) \mathbf{d}\mathbf{r} + c.c. = 0, \quad (18)$$

which would lead to

$$\varphi_i(\mathbf{r}) \left\{ \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} - \omega_{\text{eff}}(\mathbf{r}) \right\} = \lambda_i \varphi_i(\mathbf{r}), \quad \forall i = 1, \dots, N \quad (19)$$

which can not be reduced to equations of the type shown in Eq. 8 since, by virtue of the chain rule, the following condition:

$$\varphi_i(\mathbf{r}) \left\{ \sum_j^N \frac{\partial \varphi_j^*(\mathbf{r})}{\partial \rho(\mathbf{r})} \frac{\partial T_s[\rho]}{\partial \varphi_j^*(\mathbf{r})} + c.c. \right\} = -\frac{1}{2} \nabla^2 \varphi_i(\mathbf{r}) \quad (20)$$

should be satisfied for both, Eqs. 19 and 8, to be valid simultaneously. However, the KS equations (8) are immediately derived when in Eq. 15, with $T_s[\rho]$ given by Eq. 16, the spinorbitals are varied under the constraints of Eq. 18. In this case the effective potential $\omega_{\text{eff}}(\mathbf{r})$ is not only local, but it must also remain constant under variations of the spinorbitals; a condition which is also implicit in the derivation of the KS equations [7, 9, 10]. Finally, a set of KS-like equations can be obtained adopting a procedure similar to that followed when the HF equations are deduced. In this case the deduced equations must be interpreted in a wider sense than Eq. 8 because the effective potential $\omega_{\text{eff}}(\mathbf{r})$ could be either a local or, such it has been stressed by Nesbet [4], a linear operator. From Eqs. 6 and 11, where all the members are considered as explicit functionals of the spinorbitals, it is easy to obtain Eq. 8 but now the effective potential is defined as:

$$\omega_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + \sum_j^N \frac{\delta E_{xc}[\rho]}{\delta \varphi_j^*(\mathbf{r})} \hat{p}_j, \quad (21)$$

where \hat{p}_j is the projector associated to the j -th spinorbital. Equation 8 with ω_{eff} given by Eq. 21 can lead to both Eqs. (2.8) and (2.22) of [2]. The latter are easily derived if $E_{xc}[\rho]$ is written as the sum of two components, as suggested in Section II.B of [2]:

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho], \quad (22)$$

with $E_x[\rho]$ equal to the definition in HF theory but evaluated with the KS spinorbitals:

$$E_x[\rho] = \sum_{ij}^N \iint \frac{\varphi_i^*(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_i(\mathbf{r}') \varphi_j(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \mathbf{d}\mathbf{r} \mathbf{d}\mathbf{r}'. \quad (23)$$

The present discussion is aimed to shed some light on some aspects that remain unclear in the framework of KS theory. The eigenvalue equations (2.8) and (2.22) proposed in [2] are rigorously supported by the arguments discussed here. The restriction of a local effective potential can in principle be removed.

Finally, and connecting with the recent discussion about the nature of the KS equations [3–13], the present results show that although the TF-type equations obtained by applying the Fréchet criteria [15–17] to the definition of $\delta E[\rho]$, see Eqs. 10, 17, are not equivalent to the KS equations, although they are closely related to each other. In fact, the Fréchet or Gâteaux functional derivatives [15–17] have their counterparts in differential calculus in the concepts of total derivative and partial derivative,

respectively. And, as it is well known, the former can be expressed in terms of the whole set of partial derivatives with respect to the basis elements.

For the KS problem discussed here it is easy to obtain the Fréchet functional derivative starting with the N Gâteaux functional derivatives when applying the constrained search [14]. Now the extremum condition for $\delta T_s[\rho]$ is written as the following set of N equations:

$$\frac{\delta T_s[\rho]}{\delta \rho_i(\mathbf{r})} = \epsilon_i - \omega_{\text{eff}}(\mathbf{r}), \quad \forall i = 1, \dots, N \quad (24)$$

which corresponds to Eqs. 11 of [7], with $v(\mathbf{r}) = \omega_{\text{eff}}(\mathbf{r})$ and $n_i = 1$. Equation 24 correspond to Gâteaux functional derivatives. On the other hand, Eq. 13 together with Eqs. 8 and 24 lead after some simple manipulations to the following relationship:

$$T_s[\rho] = \frac{1}{N} \int \rho(\mathbf{r}) \sum_i^N \frac{\delta T_s[\rho]}{\delta \rho_i(\mathbf{r})} d\mathbf{r}. \quad (25)$$

Assuming that $\omega_{\text{eff}}(\mathbf{r})$ is kept constant when the spinorbitals are varied, a condition implicit in [7] when obtaining Eq. 24, the equality

$$\frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} = \frac{1}{N} \sum_i^N \frac{\delta T_s[\rho]}{\delta \rho_i(\mathbf{r})} \quad (26)$$

is obtained. Equation 26 coincides with the result obtained by Lindgren y Solomonson (Eq. 21 of [10]) for a system of independent particles (with $E = \sum_i^N \epsilon_i$), which shows the relationship between the Fréchet derivative and the N Gâteaux derivatives. The equality between Eqs. 26 and 21 of [10] shows the equivalence between the two procedures followed in both references [7, 10] to incorporate the normalization conditions in the variational optimization of the energy.

3 The exchange potential in a correlation-free Kohn–Sham theory

The validity of the hypothesis of a KS local potential has been also recently discussed by comparing the results between the HF and the KS solution on a set of atomic systems [4, 5, 18, 19]. Note that the discussion is done for a correlation-free KS model in which $E_{xc}^{\text{KS}} = E_x^{\text{KS}}$ and, consequently, the hypothesis of locality for the effective potential is reduced to the locality of the exchange potential; i.e., the last term of Eq. 21 with $E_c[\rho]$ of Eq. 22 taken as zero. For a correlation-free theory, where the energy corresponds to the solution of Eq. 1 with Ψ given by a Slater determinant, the ground state of the reference interacting system is described by the Hartree–Fock solution.

Additionally, it has been also found how the values of Eq. 1 obtained by using the KS Slater determinant, the

Optimized Effective Potential (OEP) method [20–25], or the HF model, systematically differ between them. The KS results correspond in this case to the correlation-free model, after assuming a local exchange potential, and the KS orbitals were obtained from the HF exact density by some of the well-rooted procedures established in the literature [6, 7, 26]. Note that in all cases the relationship $E^{\text{KS}} > E^{\text{OEP}} > E^{\text{HF}}$ was observed; the exception being the ground state of the Helium atom since for this system the exchange energy is exactly half of the electronic repulsion energy and thus the exchange potential is strictly local. The differences found between the energy values are not believed to come from numerical errors and, therefore, Nesbet and Colle [5] concluded in their study that the exchange potential does not need to be of a local nature. They also proposed a method to analyze the locality of the KS solution through the value of the integral $Q(Z)$, see Eq. 15 of [5], leading to the conclusion that the locality hypothesis is not supported by the results of the calculations. The use of $Q(Z)$ as a robust test to analyze the locality of the KS solution has been, however, rejected by other authors [9].

For a correlation-free theory, the KS hypothesis implies:

$$\rho^{\text{KS}}(\mathbf{r}) = \rho^{\text{HF}}(\mathbf{r}), \quad (27)$$

where the corresponding densities are given by:

$$\rho^{\text{KS}}(\mathbf{r}) = \sum_{\sigma} \sum_i^{N_{\sigma}} \phi_{i\sigma}^{\text{KS}*}(\mathbf{r}) \phi_{i\sigma}^{\text{KS}}(\mathbf{r}), \quad (28)$$

$$\rho^{\text{HF}}(\mathbf{r}) = \sum_{\sigma} \sum_i^{N_{\sigma}} \phi_{i\sigma}^{\text{HF}*}(\mathbf{r}) \phi_{i\sigma}^{\text{HF}}(\mathbf{r}), \quad (29)$$

and $\phi_{i\sigma}(\mathbf{r})$ is the σ spin-indexed i th-occupied orbital. These orbitals (KS or HF) are also used to build the associated Slater determinants. Note that according to this condition, both set or orbitals will be related by an unitary transformation through the corresponding matrix $\mathbf{U}_{\text{HF}}^{\text{KS}}$:

$$\Phi^{\text{KS}} = \mathbf{U}_{\text{HF}}^{\text{KS}} \Phi^{\text{HF}}, \quad (30)$$

where Φ^x represents the vector formed by the N -occupied spinorbitals defining the corresponding Slater determinant. So that, the KS hypothesis implies that both sets of KS and HF occupied orbitals transform between them by blocks characterized by a common spin. The implication of this feature is that the KS and HF one-electron density matrices are also the same and thus the value of $\langle \Phi | \hat{H} | \Phi \rangle$, with \hat{H} given by Eq. 14. The same is also true for each component of the total energy. The KS hypothesis on the density also implies a specific relation between the exchange potential of Eqs. 21, 22, taken as local, and the non-local HF exchange operator, \hat{k}^{HF} defined through its action on $\phi_j(\mathbf{r})$ as:

$$\hat{k}^{\text{HF}} \phi_{j\sigma}(\mathbf{r}) = \sum_{\sigma'} \sum_{i\sigma'}^{N_{\sigma'}} \delta_{\sigma\sigma'} \int \frac{\phi_{i\sigma'}^*(\mathbf{r}') \phi_{j\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \phi_{i\sigma'}(\mathbf{r}). \quad (31)$$

In fact, if in the following equation:

$$\sum_{\sigma} \sum_i^{N_{\sigma}} \epsilon_{i\sigma}^{\text{KS}} = \sum_{\sigma} \sum_i^{N_{\sigma}} \left\langle \phi_i^{\text{KS}} \left| -\frac{1}{2} \nabla^2 + \omega_{\text{eff}}(\mathbf{r}) \right| \phi_i^{\text{KS}} \right\rangle \quad (32)$$

the HF operator is added and subtracted into the bracket, we immediately arrive to

$$\int v_x^{\text{KS}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} = - \sum_{\sigma} \sum_i^{N_{\sigma}} \int \phi_{i\sigma}^*(\mathbf{r}) \hat{k}^{\text{HF}} \phi_{i\sigma}(\mathbf{r}) d\mathbf{r} + \Delta, \quad (33)$$

with

$$\Delta = \sum_{\sigma} \sum_i^{N_{\sigma}} (\epsilon_{i\sigma}^{\text{KS}} - \epsilon_{i\sigma}^{\text{HF}}), \quad (34)$$

and v_x^{KS} the corresponding local KS exchange potential. Equation 33 establishes a direct relationship between the action of the KS exchange potential and the non-local exchange operator of HF theory. Only if $\Delta = 0$ the KS exchange potential, which is a local potential by construction, and the HF exchange operator, which is the true non-local potential, will be equivalent.

We show in Table 1 some numerical examples of results from correlation-free calculations. More specifically, Table 1 gathers the ground-state energies, as well as the

Table 1 Total (E) and one-electron (ϵ) energies (in a.u.) for He, Be, and Ne atoms calculated with different exchange-only theories

Atom	HF ^a	OEP ^a	xS ^a	B88 ^b	KS ^a
He					
E	-2.8617	-2.8617	-2.8617	-2.8608	-2.8617
ϵ_{1s}	-0.918	-0.918	-0.918	-0.549	-0.918
$\sum_i \epsilon_i$	-0.918	-0.918	-0.918	-0.549	-0.918
Be					
E	-14.5730	-14.5725	-14.5614	-14.5639	-14.5724
ϵ_{1s}	-4.733	-4.123	-4.624	-3.877	-4.125
ϵ_{2s}	-0.309	-0.311	-0.326	-0.181	-0.309
$\sum_i \epsilon_i$	-5.042	-4.434	-4.950	-4.058	-4.434
Ne					
E	-128.5471	-128.5455	-128.5007	-128.5693	-128.5454
ϵ_{1s}	-32.772	-30.710	-32.076	-30.488	-30.821
ϵ_{2s}	-1.931	-1.602	-1.751	-1.294	-1.7120
ϵ_{2p}	-0.850	-0.733	-0.912	-0.456	-0.852
$\sum_i \epsilon_i$	-37.253	-34.511	-35.653	-33.150	-35.097

^a Taken from [6]

^b Done here with the 6-311++G** basis sets and the ORCA package [76]

orbital energies and their sums, for the closed-shell He, Be, and Ne atoms. We compare several exchange-only theories, as described above: HF, OEP, exchange Slater potential (xS) [27, 28] defined by:

$$V_{\text{xS}}^{\sigma}(\mathbf{r}) = -\frac{1}{\rho_{\sigma}(\mathbf{r})} \sum_{ij}^{N_{\sigma}} \int \frac{\phi_i^*(\mathbf{r}) \phi_j^*(\mathbf{r}') \phi_j(\mathbf{r}) \phi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (35)$$

and approximate KS results based on the B88 exchange functional [29], which is probably the most well-known example of a Generalized Gradient Approximation exchange energy functional. The exact KS results are also included; the latter were obtained by using the HF density and iteratively solving for the $v_x(\mathbf{r})$ until self-consistency by enforcing the condition $\rho(\mathbf{r}) = \rho^{\text{HF}}(\mathbf{r})$ in each step of the convergence process followed to obtain the KS orbitals [26]. From Table 1 the values of Δ , as given by Eq. 34, 0.608 and 2.156 a.u., for Be and Ne, respectively, are readily obtained; they indicate the non-equivalence between the local KS and the HF exchange potential, in agreement with previous findings [4–6].

Furthermore, according to the above discussion about the equivalence of both set of occupied KS and HF orbitals, the corresponding KS and HF energies, as well as their components, should be the same, which is not observed from the values shown in Table 1. All the features discussed above points to the fact that a correlation-free theory with a local effective potential and providing the HF density is not feasible at all, despite the fact that the procedure followed to obtain the KS results leads to values very close to the HF ones. The closeness between both results might indeed hide any difference between the output (KS) and the input (HF) densities. Note that the overlap between KS and HF wavefunctions obtained in [4] seems to corroborate this conclusion.

4 The semi-integrated expression of the exchange energy

According to the foundations of DFT theory, we start by writing a generalized exchange energy functional as:

$$E_x^{\text{DFT}} = \iint e_x[\rho(\mathbf{r}), \rho(\mathbf{r}'), \rho'(\mathbf{r}), \rho'(\mathbf{r}'), \dots] d\mathbf{r} d\mathbf{r}' \quad (36)$$

where $\rho(\mathbf{r})$ and $\rho'(\mathbf{r})$ are the density and its first derivative. Note that Eq. 36 stresses the non-local nature of the exact exchange energy. As a matter of fact, in HF theory the above expression is merely written in terms of the orbitals, as in Eq. 23. In the framework of a gradient corrected approximation, GGA and further extensions thereof, the exchange energy is written as a local functional:

$$E_x^{\text{GGA}} = \int e_x^{\text{GGA}}[\rho(\mathbf{r})]d\mathbf{r}, \quad (37)$$

although, admittedly, $e_x^{\text{GGA}}[\rho(\mathbf{r})]$ might include an explicit dependence on a variety of gradient-like corrections ($\nabla\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|^n, \nabla^2\rho(\mathbf{r}),$ etc) which thus include the most common approximations up to the fourth rung of Jacob's ladder [30]. Let us suppose now that the latter equation intends to mimic the features of Eq. 36, in that case:

$$e_x^{\text{GGA}} = \int e_x[\rho(\mathbf{r}), \rho(\mathbf{r}'), \rho'(\mathbf{r}), \rho'(\mathbf{r}'), \dots]d\mathbf{r}', \quad (38)$$

while the corresponding exchange potentials are defined by the functional derivation of both forms, $\frac{\delta E_x^{\text{DFT}}}{\delta\rho}$ and $\frac{\delta E_x^{\text{GGA}}}{\delta\rho}$. Thus, the potentials obtained by the two different paths are not equivalent, as we will show later, and this feature might explain the wrong behavior experienced by all the GGA or meta-GGA exchange potentials obtained as the functional derivative of a semi-integrated expression.

In fact, let us consider for the sake of simplicity the following functional:

$$F[f] = \int f(x)k[f(x)]dx, \quad (39)$$

where $k[f(x)]$ is an unknown functional of $f(x)$. The variational derivative of the above equations is:

$$\frac{\delta F[f]}{\delta f} = k[f(x)] + \int f(x'')\frac{\delta k[f(x'')]}{\delta f(x)}dx''. \quad (40)$$

Taking for $k[f(x)]$,

$$k[f(x)] = \int f(x')h(x, x')dx', \quad (41)$$

where $f(x)$ is a continuous and derivable function in the whole interval of integration and $h(x, x')$ is a function that does not depend on f , and making the adequate changes in the indexes, the functional derivative of $F[f]$ would finally read as:

$$\frac{\delta F[f]}{\delta f(x)} = 2 \int f(x')h(x, x')dx'. \quad (42)$$

On the other hand, if $k[f(x)]$ is explicitly integrated over x' , and the resulting function $g(x)$ is inserted into Eq. 39, we arrive at the semi-integrated (SI) expression:

$$F^{\text{SI}}[f] = \int f(x)g(x)dx. \quad (43)$$

Note that $g(x)$ here can be also a function of $f(x)$, such as it happens in the example given in next subsection. Hence, the functional derivative must be written as [31, 32]:

$$\frac{\delta F^{\text{SI}}[f]}{\delta f(x)} = g(x) + f(x)\frac{\partial g(x)}{\partial f(x)}, \quad (44)$$

which generally differs from Eq. 42; the equality of both results are obviously obtained if $h(x, x') = \delta(x - x')$, where $\delta(x - x')$ is the Dirac delta function. We can thus clearly established at this stage that the two ways followed to obtain the functional derivative are not fully equivalent.

4.1 A simple model for atomic systems

For a closed-shell two-electron system, such as the ground state of the Helium atom, the exchange energy is:

$$E_x[\rho] = -\frac{1}{4} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}d\mathbf{r}', \quad (45)$$

which following Eq. 40 leads to the corresponding exchange potential,

$$v_x[\rho] = -\frac{1}{2} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}'. \quad (46)$$

Let us suppose that the density of the ground-state of the Helium atom is represented by an hydrogen-like function such as:

$$\rho(\mathbf{r}) = N\frac{\xi^3}{\pi}e^{-2\xi r}, \quad (47)$$

where N and ξ are the number of electrons and the effective nuclear charge, respectively. This model density has been repeatedly used in theoretical studies of exchange-correlation functionals and their formal properties [33–38]. If we resort to the expression of $|\mathbf{r} - \mathbf{r}'|^{-1}$ in terms of the associated spherical harmonics, and the subsequent integration of the \mathbf{r}' coordinate, it is easily verified that Eq. 46 transforms to:

$$v_x[\rho] = -\frac{\pi}{2r\xi^3} \left[\frac{N\xi^3}{\pi} - \rho(r)(1 + \xi r) \right]. \quad (48)$$

On the other hand, the functional derivative of the semi-integrated expression for $E_x[\rho]$:

$$E_x^{\text{SI}}[\rho] = \frac{1}{2} \int \rho(\mathbf{r})v_x[\rho]d\mathbf{r}, \quad (49)$$

has as a result:

$$v_x^{\text{SI}}[\rho] = v_x[\rho] + \frac{N}{4r}. \quad (50)$$

Figure 1 shows how the potentials given by Eqs. 48 and 50 evolve as a function of the distance from the nucleus for a value of ξ (1.6395) for which the energy reaches its optimum value. We remark how the potential obtained from Eq. 48 exhibits all the features of the exact exchange potential, particularly its finiteness at both limits (-2ξ for $r \rightarrow 0$ and 0 for $r \rightarrow \infty$). Note that the small differences with respect to the exact potential, Eq. 46 with $\rho(\mathbf{r})$ obtained from [39], are attributed to the use of an

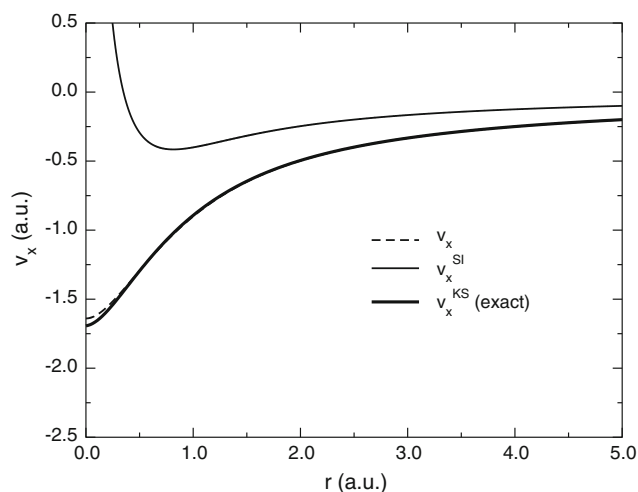


Fig. 1 Plot of the v_x and the v_x^{SI} of Eqs. 48 and 50, as a function of r and using Eq. 47, together with the exact exchange potential v_x^{KS} evaluated by Eq. 48 and the density taken from [39]

approximate density at this stage. On the other hand, $v_x^{SI}[\rho]$ diverges at the origin and leads to an asymptotic trend different from the exact one.

4.2 Features of common exchange potentials

Considering the preceding results, it is now turn to discuss the application of a wide set of the GGA exchange potentials [30, 40, 41] obtained as the functional derivative of the corresponding local exchange functional. The chronologically ordered sample of the Sham–Kleinman (SK71) [42, 43], Langreth–Mehl (LM83) [44], Perdew–Wang (PW86, PW91) [45–47], Becke (B86, B88) [29, 48, 49], OuYang–Levy (OYL91) [50, 51], Engel–Chevary–MacDonald–Vosko (ECMV92) [52], Lacks–Gordon (LG93) [53], Gill (G96) [35], Perdew–Burke–Ernzerhof in both the original (PBE96) [54] and revised versions (r-PBE96, [55] and RPBE96 [56]), and Tozer–Handy (TH98) [57] models are chosen. Figure 2 compares the exchange potential with the exact expression obtained again from Eq. 46. For the sake of clarity, only the LDA, B88, and OYL91 results are shown. A subset from the whole set of potentials (LM83, SK71, and G96) behaves very similarly to the OYL91 while the rest of them are very close to B88. All the calculations were made using the density obtained from the correlated Roothaan–Weiss wavefunction [39], which has been shown to be accurate enough in the determination of DFT quantities for this two-electron system [58, 59]. We observe several important features in close agreement with previous studies [41, 60]: (a) All the GGA potentials diverge at the nucleus; (b) the asymptotic limit of the exact potential ($-1/r$) at large distances is not reached by any of the expressions and some of them even diverges or show spurious minimum, and (c)

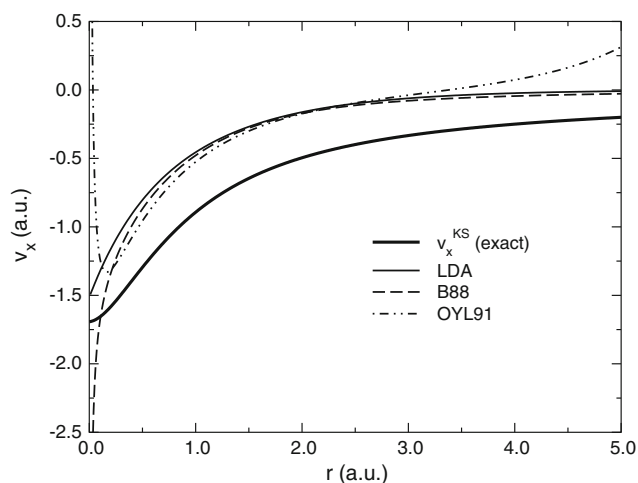


Fig. 2 Comparison of various approximate GGA exchange potentials with the exact expression of Fig. 1

all the models have very similar shapes in the intermediate region and are qualitatively wrong. We would like to underline that all the expressions derived from a semi-integrated model seems to share the same drawbacks independently of the constraints and/or parameters entering into the model. Note that we do not consider at this stage the new generation of functionals that include higher derivatives of the density [61–65]. We have previously shown [66] that the semi-integrated form, even if it is expanded in a Taylor series to include dependences on higher derivatives of the density, does not converge to the exact solution; thus, the results exposed here are believed to be largely independent of the density functional employed.

We continue with some numerical tests to complement the previous conclusions. If $v_x[\rho]$ is the functional derivative of the exact functional for the exchange energy, the following relation (derived from the virial theorem) between $v_x[\rho]$ and $E_x[\rho]$ is accomplished [67, 68]:

$$E_x^{\text{virial}}[\rho] = - \int \rho(\mathbf{r}) \mathbf{r} \cdot \nabla v_x[\rho] d\mathbf{r} \\ \equiv \int [3\rho(\mathbf{r}) + \mathbf{r} \cdot \nabla \rho(\mathbf{r})] v_x[\rho] d\mathbf{r}. \quad (51)$$

The results from the use of the latter expression are expected to confirm the previous reasoning. If $v_x[\rho]$ and $\rho(\mathbf{r})$ are known exactly, the relation must give the exact value for E_x [37, 69, 70]. Table 2 presents the value of this

Table 2 Comparison of the exchange energy (in a.u.) provided by the virial expression

	E_x	$v_x[\rho]$	$v_x^{SI}[\rho]$
He	-1.0247	-1.0247	0.6148

The exact result is the number given in the first column

integral when $v_x[\rho]$ (Eq. 48) and $v_x^{SI}[\rho]$ (Eq. 50) are inserted together with the density given by Eq. 47. It is easily seen how $v_x[\rho]$ provides the exact value for the exchange energy; however, the same cannot be affirmed for $v_x^{SI}[\rho]$, which clearly show again the non-equivalence of both procedures. We also note that the Ayers–Levy sum rule [71] for the exchange potential:

$$4\pi = \int d\mathbf{r} \nabla^2 v_x[\rho], \quad (52)$$

does not allow to discriminate between the exact ($v_x[\rho]$) and the semi-integrated ($v_x^{SI}[\rho]$) form since the asymptotic decay of both potentials is correct to order $1/r$ in the limit of large r .

Table 3 lists next the results obtained now when an approximate GGA potential is inserted into Eq. 51. The first column lists the exchange energy as provided by an accurate integration of the labeled functional, whereas the values obtained from the inclusion of the corresponding GGA potentials into Eq. 51 are under the header $E_x^{\text{virial}}[\rho]$. The rest of the columns collect the relative errors with respect to the exact value. The results are fully consistent with the above conclusion; i.e., the exchange potentials usually employed for the resolution of the KS one-electron equations are associated to expressions that aim to reproduce the semi-integrated form of the exact exchange energy and, therefore, cannot truly represent the exact exchange potential. Amazingly, all the approximate models behave reasonably well for the evaluation of the exchange energy of the

system, as can be confirmed from further inspection of Table 3. Despite the wrong behavior at all distances, mainly at both the nucleus and asymptotic limits [72, 73], accurate values are obtained for several functionals. For instance, OYL91 provides roughly the same value for the exchange energy either by integration of the corresponding energy density or by inserting the corresponding functional into Eq. 51. On the other hand, the well-known B88 functional gives a very accurate value when integrated but largely deteriorates when the energy is evaluated through Eq. 51. Thus, the good values obtained might be possibly attributed to a subtle cancellation of local errors [74]. The LDA functional is an exception since this is a local functional by its own construction which thus does not belong to any semi-integrated form of a non-local functional. Hence, the potential obtained by functional derivation should satisfy Eq. 51, as is indeed the case. In view of these results, we might reasonably state that the main reason for the generalized failures of the DFT exchange potentials is the use of a semi-integrated expression of the exchange energy to obtain the associated potentials, even if the integrand is well-fitted to reproduce with the highest accuracy the integrand of the exact semi-integrated form.

5 Conclusions

A set of important aspects within the current DFT framework, under which the majority of exchange energy functionals and associated exchange potentials are formulated, have been thoroughly discussed. We tackle a combined approach in which purely theoretical reasonings, together with analytical soluble models which are considered to serve as benchmark systems for the development of approximated but accurate and manageable approximations, are first considered and then further supported by complementary numerical proofs. We have first discussed the variational problem associated to the KS equations, and the non-equivalence between the local exchange potential of KS theory and the non-local exchange potential of the HF theory in order to conclude that a correlation-free KS theory having a local exchange potential able to provide the exact HF density seems not to be feasible. We have shown, through a combination of integrated values and point-wise quantities, the inability for GGA-based approximate exchange potentials to reproduce the characteristics of the exact exchange potential; this drawback being related with their derivation from expressions which are local in nature. As a by-product, the use of only integrated quantities when developing theoretical procedures seems to be not highly recommended since the integrated magnitudes may not fully represent the complexity of the problem [75].

Table 3 The exchange energy (in a.u.) of the He atom evaluated from approximate GGA exchange functionals ($E_x^{\text{GGA}}[\rho]$) and by inserting the corresponding GGA-derived potentials in the virial expression ($E_x^{\text{virial}}[\rho]$)

	$E_x^{\text{GGA}}[\rho]$	δ_r	$E_x^{\text{virial}}[\rho]$	δ_r^{virial}
LDA	-0.8836	-13.8	-0.8835	-13.8
SK71	-1.0061	-1.82	-1.0054	-1.89
LM83	-1.0140	-1.04	-1.0132	-1.12
PW86	-1.0328	0.79	-1.0418	1.67
B86	-1.0270	0.47	-1.1790	15.1
B88	-1.0252	0.04	-1.0092	-1.52
OYL91	-1.0278	0.29	-1.0280	0.32
PW91	-1.0162	-0.84	-1.0234	-0.13
ECMV92	-1.0255	0.08	-1.0336	0.86
LG93	-1.0279	0.30	-1.0378	1.28
G96	-1.0280	0.32	-1.1022	7.56
PBE96	-1.0134	-1.11	-1.0210	-0.36
r-PBE96	-1.0284	0.36	-1.0011	-2.30
RPBE96	-1.0310	0.62	-1.0402	1.51
TH98	-1.0979	7.14	-1.2930	26.2

The corresponding signed relative error (δ_r and δ_r^{virial} , both in %) with respect to the exact value is also shown

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