
Adiabatic Connection Approach to Density Functional Theory of Electronic Systems

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Received 21 March 2002; accepted 8 January 2003

DOI 10.1002/qua.10551

ABSTRACT: Using recent calculations we review some well-known aspects of density functional theory: the Hohenberg–Kohn theorems, the Kohn–Sham method, the adiabatic connection, and the approximations of local nature. Emphasis is put upon using model Hamiltonians, of which the noninteracting or the physical ones are just particular cases. The model Hamiltonians allow us to produce multireference density functional theory and continuously switch to the physical system. © 2003 Wiley Periodicals, Inc. *Int J Quantum Chem* 93: 166–190, 2003

Key words: Kohn–Sham method; density functional theory; adiabatic connection; approximations

Introduction

The density functional (DF) approach relies on minimizing an expression for the total energy for a given local external potential v (as a rule that of the nuclei) in which the N electrons move, $E[N, v] = \min_n \{F[n] + \int v n\}$. Only the electron density, n , integrating to N (and not the wave function) enters into the expression of the energy. Further, the functional $F[n]$ depends on the electron density n alone. The minimizing density is the ground-state density of the system described by the potential v . In the Kohn–Sham (KS) method, the functional $F[n]$ is de-

composed in a way that transforms this minimization problem to become equivalent to that of a system of independent particles. An adiabatic connection in DF theory (DFT) continuously transforms this independent particle system to the physical one.

Highly successful applications of DFT made it now probably the most popular method in quantum chemistry despite the constraint of using approximations for $F[n]$. At the same time, the increasing accuracy demand requires also improving on the existing approximations for $F[n]$. Further, more and more attention is devoted to applying this approach not only for energies, densities, and quantities derived from them but also to other properties. These efforts, of course, encourage thinking about fundamental aspects of DFT. Some of them will be

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highlighted in this article. We will also try to point out to some efforts to go beyond the independent-particle model of Kohn and Sham.

We imposed a few limitations to this article. One of them is the literature cited. The references given are just examples, and other relevant important articles exist. The references quoted do not even cover the whole domain of research of the authors. We would like to quote at this point a few books, series, and reviews dedicated to DFT: [1–33]. It is difficult to recommend a book or a review article. In our experience, mathematically inclined people like the book by Eschrig [2], those who like physics that of Dreizler and Gross [1], while chemists often prefer the book of Parr and Yang [6] or that of Koch and Holthausen [3] (for those having a penchant toward fundamental aspects, or applications, respectively). Many details can be found in the book by Kryachko and Ludeña [4], while a good rapid introduction is, e.g., given in the article by Perdew and Kurth [34]. An inspiring lecture is the book by March [5].

Another limitation of this article is that the proofs were at most sketched, as going through the details would make the article more difficult to read. The interested reader can find the proofs in the literature.

The article has three parts: First, the fundamental theorems by Hohenberg and Kohn are discussed; second, the KS method is presented, together with adiabatic connections; last, the way to introduce approximations, and some of their effects, are discussed.

The calculations presented were performed using the program Molpro [35] and with *Mathematica* [36].

Hohenberg–Kohn Approach: Universal Density Functional

DENSITY AND POTENTIAL

Usually, quantum mechanics is taught by showing the need to have a wave function to describe an electronic system. However, textbooks mention, too, that to obtain the energy of an electronic system, and many of its properties, the wave function is not needed; one only has to know the second-order reduced density matrix and the potential in which the electrons move. Writing the energy in terms of the second-order density matrix is immediate; the only real problem is how to guarantee

that a wave function exists that yields the trial density matrix. In recent years, this point of view has received new impulses and has shown encouraging results as a way to construct good approximations (see, e.g., [37–40]). In contrast to this approach, the celebrated work of Kohn and coworkers [41, 42] emphasizes the role of the (one-particle) electron density. In this approach, there is no problem generating a physically correct trial density; the prescription how to obtain the energy is again exact, but this time only in principle, as the exact functional dependence on the density is not known.

Let us consider an electronic system in an external potential $\nu = \nu(r)$ (the interaction of the electrons with the external field, e.g., that of the nuclei). Let its ground-state density be $n_\nu = n_\nu(r)$, integrating to N , the number of electrons. All the properties of the system can be obtained by the knowledge of the Hamiltonian of that system, which is immediately written down once N and ν are given. The properties are thus functionals of ν and N , as, for example, the ground-state energy, $E[N, \nu] = \min_\Psi \langle \Psi | H_{\nu, N} | \Psi \rangle$. As n_ν is defined to yield by integration N , the properties of an electronic system can be obtained from the knowledge of n_ν and ν . For example, the ground-state energy can be obtained by the knowledge of n_ν and ν : There exists a functional $E[n_\nu, \nu]$ yielding $E[N, \nu]$.

Hohenberg and Kohn [41] showed that for a given ground-state density n the local potential ν that generates it is uniquely determined. Thus, the knowledge of n is sufficient to determine all the properties of an electronic system described by a Hamiltonian $T + V_{ee} + V$. Unique means, in the present context, up to an arbitrary constant. (This is related to the arbitrariness in the choice of the zero of energy.)

For more general forms of the Hamiltonian, e.g., when a magnetic field is present, this statement does not remain necessarily true [43, 44]: The ground-state density may not change with the magnetic field, so one comes back to the statement that both n and the interaction with the external potential are needed to obtain E . This does not seem an important handicap from the authors' viewpoint: When a given system is analyzed, the potential is known, anyhow. Note, however, that some statements of the DFT literature rely on the uniqueness of the potential.

The HK theorem does not state that a ground-state density $n_\nu + \delta n$, where δn is small, comes from a potential $\nu + \delta \nu$, where $\delta \nu$ is small.

A simple example of a large change in the potential that produces only a small change in the density was provided by Levy [45]. He considers a shift by a constant in the physically (numerically relevant region) but not in the asymptotic region. Similarly, adding a rapidly oscillating potential to the exact one will produce only vanishingly small changes to the potential, even if the amplitude of the oscillations is large. As Kohn puts it [46]: The particle does not see the rapid oscillations of the potential. These examples seem to be only of academic interest. One has to consider, however, that we almost never have the “exact” density: It most often comes from some basis set calculation. Thus, for almost all cases we can treat explicitly there is a δn due to the finite basis set. It turns out that $\delta\nu/\nu$ is usually one to two orders of magnitude larger than $\delta n/n$ [47]. Figure 1 shows the three types of slight changes of the potential for the hydrogen atom. In Figure 2 the relative error of the potential is compared to that in the density for a commonly used Gaussian basis set.

To understand the origin of this problem, one may consider the change of the density as given by perturbation theory [49]. In a compact notation, $\delta n(r)$ is connected to $\delta\nu(r')$ via

$$\delta n(r) = \int \chi(r, r') \delta\nu(r') d^3r', \quad (1)$$

where the response function $\chi(r, r')$ is given, in the sum-over-states form, for real functions by

$$\chi(r, r') = 2 \sum_{i(\neq 0)} \langle \Psi_0 | \hat{n}(r) | \Psi_i \rangle \times \langle \Psi_i | \hat{n}(r') | \Psi_0 \rangle / (E_0 - E_i), \quad (2)$$

where the energies E_i and the eigenfunctions Ψ_i are those of the Hamiltonian with potential ν ; $\hat{n}(r) = \sum_{i=1,N} \delta(r - r_i)$ is the density operator.

The response function can be written in terms of its (orthonormal) eigenfunctions ψ_i and eigenvalues, κ_i :

$$\chi(r, r') = \sum_i \kappa_i \psi_i(r) \psi_i(r') \quad (3)$$

For the hydrogen atom, the absolute values of the κ_i are lying between 10^{-1} and 0, the absolute values decreasing with the number of nodes in ψ_i , those having the largest $|\kappa_i|$ being shown in Figure 3 [50].

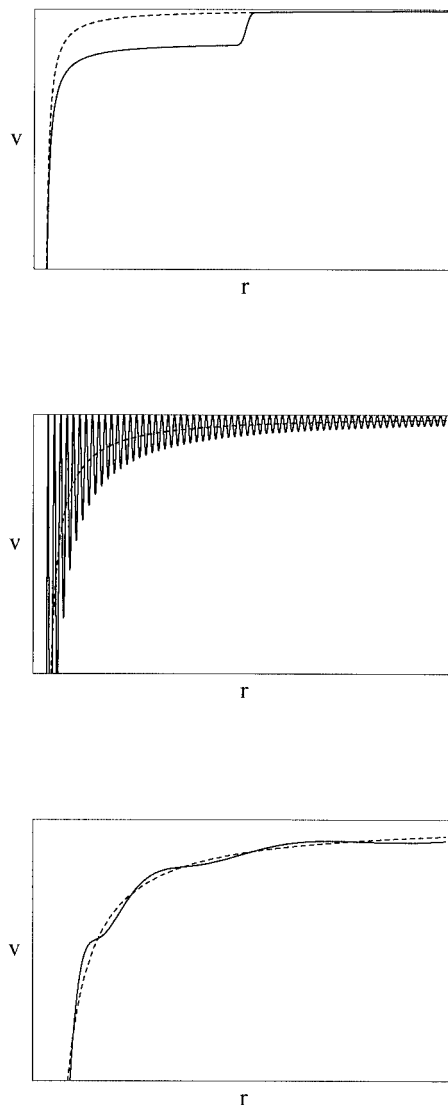


FIGURE 1. Hydrogen atom potential ($-1/r$, broken curve) (1) modified by a shift by a constant over the physically significant region, (2) modified by adding rapid oscillations, or (3) reproducing the density obtained from a variational calculation with the physical potential using a Gaussian basis set (four Gaussian functions [48], yielding an energy error of 0.1%).

Expanding $\delta\nu$ in terms of the $\psi_i(r)$,

$$\delta\nu(r) = \sum_i \nu_i \psi_i(r) \quad (4)$$

and using the equations above, it turns out that the expansion coefficients of $\delta n(r)$, in terms of the ψ_i , are $\kappa_i \nu_i$:

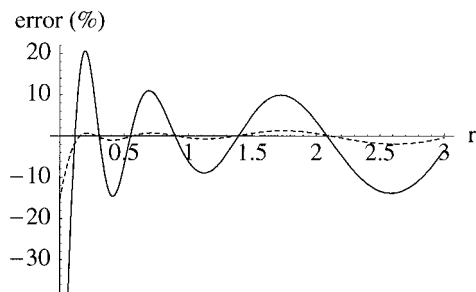


FIGURE 2. Relative errors in the density (broken curve), and in the potential generated from this density (full curve), produced by using a common Gaussian basis set (four Gaussian functions [48], yielding an energy error of 0.1%), as a function of the radial distance, in bohr, for the hydrogen atom.

$$\delta n(r) = \sum_i \kappa_i v_i \psi_i(r). \quad (5)$$

Thus, a change in the potential equal to $\delta v(r) = \epsilon \psi_i(r)$, where ϵ is a small number, yields a density change $\delta n(r)$ with one non-zero $n_i = \epsilon \kappa_i$. Thus, if κ_i is small a relatively large change in the potential v_i can be produced by a much smaller change in the density n_i . For the hydrogen atom, for example, a perturbation of the density having the shape of ψ_3 (shown in Fig. 3) produces a change in the potential two orders of magnitude larger than that in the density.

This discussion points out to two aspects in the construction of (e.g., KS) potentials starting with a given (approximate) density. The negative aspect is that special care is needed in practice when the correct v has to be produced from a given n . The positive aspect is that even poor potentials may work well, as the error in the potential may propagate only little to changes in the density (large v_i are multiplied with small κ_i , yielding small n_i).

In the case of degeneracy, there may be different densities, say, n_1 and n_2 , associated with the same potential v . The difference between n_1 and n_2 can be large. As an example, one may think of an atom having a singly occupied p_x or p_y orbital. By appropriately choosing a small δv_1 the resulting density, $n_1 + \delta n_1$, is close to n_1 , while with another small δv_2 the resulting density, $n_2 + \delta n_2$, is close to n_2 . Consider now a small change in the potential from $v + \delta v_1$ to $v + \delta v_2$. The change in the potential is small, $\delta v_2 - \delta v_1$, but the change in the density produced by it, $n_2 - n_1 + \delta n_2 - \delta n_1$, is not small.

The appearance of an additional system far from the system under consideration can produce impor-

tant changes in the density. Consider, e.g., a H atom. The presence of a He^+ ion produces a ground state in which the electron is transferred from the H atom to the He^+ ion, as $\text{H}^+ \cdots \text{He}$ is more stable than $\text{H} \cdots \text{He}^+$; the ionization potential of He is larger than that of H. To keep the density that of $\text{H} \cdots \text{He}^+$, a different potential is needed. It is essentially that produced by shifting the potential of He upward by a constant equal to the difference between the two ionization potentials to prohibit the electron transfer from one system to the other. Figure 4 shows the potential obtained for independent particles, yielding the density given by the wave function obtained by antisymmetrizing and normalizing the product of the H and the He^+ eigenfunction, 100 a.u. apart. (Note also that the asymptote is determined by the H atom having a more diffuse density than the He^+ ion.)

UNIVERSAL FUNCTIONAL AND VARIATIONAL PRINCIPLE

Hohenberg and Kohn (HK) prove that there exists a functional of n alone, (a “universal” functional, independent of v , that characterizes a specific system), $F[n]$, such that the functional $E[n, v] = F[n] + \int v n$, for a given “external” potential $v = v(r)$ reaches its minimum for the ground-state density n_v of the system characterized by the external potential v and having a number of electrons $N = \int n_v$.

Of course, for a given physical v the value of $F[n_v]$ can be directly obtained from $E[N, v] - \int v n_v$. The functional $F[n]$ can be obtained also when v is not known by the following prescription: $F[n] =$

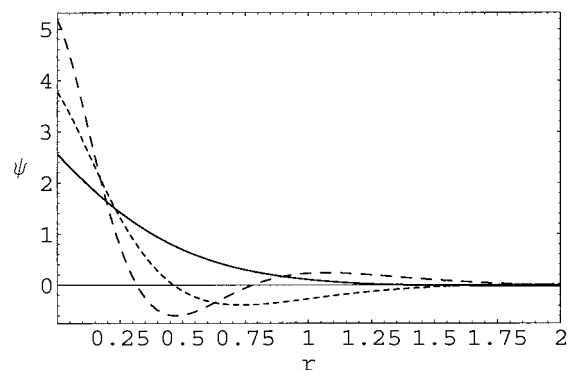


FIGURE 3. Eigenvectors ψ_i of the static density-density response function $\chi(r, r')$, for the hydrogen atom, as a function of the radial distance r , corresponding to the eigenvalues -0.123 , -0.024 , and -0.011 (full, short-broken, and long-broken curves, respectively) (a.u.).

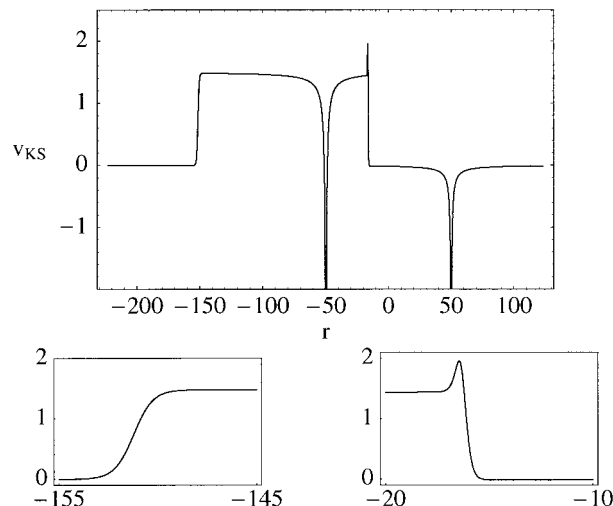


FIGURE 4. Representation of the shift of the potential by a constant in one region of space: independent particles yielding the density of H, right, and of He^+ , left, 100 a.u. apart, (antisymmetrized, normalized product). The smaller plots in the lower part of the figure are enhancements in the region where the potential makes jumps. The upward displacement of the potential around the center with $Z = 2$ is of ≈ 1.5 a.u. and makes its lowest energy level degenerate with that in the well of $Z = 1$.

$\max_{\tilde{v}} \{E[N, \tilde{v}] - \int \tilde{v}n\}$ ([51]; see also [41, 52–55]).* When the density n is the ground state of a system with potential v , $n = n_v$, the maximizing \tilde{v} is equal to v . Thus, finding $F[n]$ corresponds in fact to finding the Hamiltonian having the ground-state density n .

We see that such a recipe requires the knowledge of $E[N, \tilde{v}]$ and thus performing expensive wave function (many-body) calculations. Thus, such a recipe is of no interest in applications of DFT despite being numerically performed in a few cases to contribute to the understanding of DFT [56–62].

For example, we show in Figure 5 the potential obtained numerically by requiring that the ground-state density should be twice that of the hydrogen atom: $n = 2/\sqrt{\pi} \exp(-2r)$ [60], thus having $N = 2$. To facilitate comparisons, the plot shows the potential multiplied by r . Of course, it is not the potential of the hydrogen atom (which would correspond in our plot to a horizontal line at -1). The potential yielding twice the hydrogen atom density must be more attractive than that of H to keep the density equal to that of the noninteracting H^- ion despite the repulsion between electrons. It presents some

*For the sake of generality, $\max_{\tilde{v}}$ has to be replaced by $\sup_{\tilde{v}}$.

similitude to the potential of the helium atom (in our plot it corresponds to a horizontal line at -2), but it has to produce a density that is—to a first approximation—more diffuse than that of He.

A transparent way of writing $F[n]$ was given by Levy [63]: $\min_{\Psi \rightarrow n} \langle \Psi | T + V_{ee} | \Psi \rangle$. Of course, when n is produced by an ensemble there is not necessarily a ground-state wave function Ψ yielding the density n [51, 64]. This type of procedure has been also followed in numerical studies [65, 66]. There is a simple generalization of this formula by considering, instead of wave functions, ensemble density matrices, $\Gamma = \sum_i \omega_i |\Psi_i\rangle \langle \Psi_i|$ yielding n , with $0 \leq \omega_i \leq 1$, $\sum_i \omega_i = 1$ [51, 64, 67, 68]:

$$F[n] = \min_{\sum_i \omega_i |\Psi_i\rangle \langle \Psi_i| \rightarrow n} \sum_i \omega_i \langle \Psi_i | T + V_{ee} | \Psi_i \rangle. \quad (6)$$

Fictitious Systems: Adiabatic Connections and the Kohn–Sham Method

ADIABATIC CONNECTIONS

The HK proof holds also if the Hamiltonian is not the physical one, e.g., by modifying the interaction between electrons. A common choice is to make the replacement $1/r_{12} \rightarrow \lambda 1/r_{12}$, with $\lambda \in [0, 1]$. Another possibility is: $1/r_{12} \rightarrow \text{erf}(\mu r_{12})/r_{12}$ with $\mu \in [0, \infty)$. Instead of changing the interaction between particles, one may introduce nonlocal one-particle operators, e.g., add $G\mathcal{P}$ with $G \in [0, \infty)$, where \mathcal{P} is a projector operator onto some model space. The action of the operator added is to shift the energies of the orbitals of the model space by

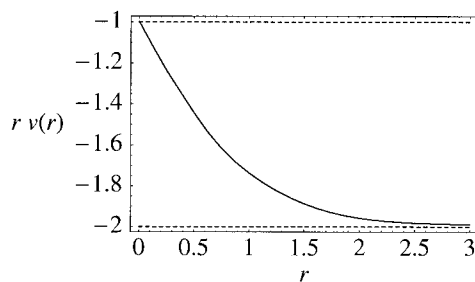


FIGURE 5. External potential producing twice the density of the hydrogen atom, multiplied by r , as a function of r (a.u.). The plots for the atomic H or He give horizontal (broken) lines at -1 and -2 , respectively. (The data were produced in accurate calculations [60].)

the constant G . The effect of these operators is shown in Figures 6 and 7.

We see that in all these examples one has families of operators, depending on some parameter, ξ , that produce at one end of its definition interval ($\lambda = 1$, $\mu \rightarrow \infty$, $G = 0$) the physical situation. At the other end, a Hamiltonian is produced for which the Schrödinger equation is supposed to be easily solved ($\lambda = 0$, $\mu = 0$: no interaction between particles; $G \rightarrow \infty$: a finite number of states to be considered).

Despite being identical at the limits of their respective domains, the action of the operators is different for intermediate values of the parameters. For example: λ/r_{12} overall weakens the physical interaction, while $\text{erf}(\mu r_{12})/r_{12}$ describes the physical long-range interaction but cuts it off to reach a constant $\mu 2/\sqrt{\pi}$ when $r_{12} = 0$, avoiding the divergence of $1/r_{12}$ at the origin.

By varying the parameter ξ one can follow the transformation of one system into the other along this “adiabatic connection.”

When modifying only the interaction, or the non-local one-body operator, the density of the system will, in general, change. However, we can modify simultaneously the external potential to keep the density constant. This can be done to an arbitrary numerical accuracy [59, 60] or by using reasonable approximations to it. The first adiabatic connection presented in the literature [69] did not keep the density constant. Later, it turned out to be formally more convenient within DFT to keep it constant [70, 71]: In such an approach, there is no need to keep track of the changes in n with ξ . Further, the electrostatic interaction is not changed with ξ . In practice, however, the exact density is not known beforehand.

It turns out that some of the proposals for modifying the external potential with ξ give good approximations to the potential keeping the density constant (see, e.g., [56–58, 61, 72, 73]). For example,

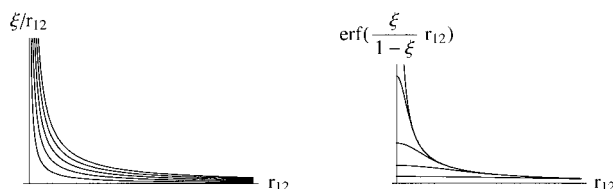


FIGURE 6. Family of electron–electron interactions ξ/r_{12} , left, or $\text{erf}[\xi/(1-\xi)]/r_{12}$, right, as a function of r_{12} , for ξ taking the values 0.2, . . . , 1. The uppermost curve corresponds to $1/r_{12}$.

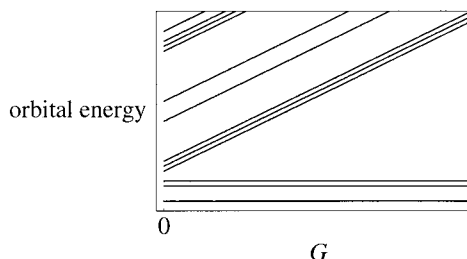


FIGURE 7. Schematic representation of the action of the operator G : It acts only on a part of the orbitals, shifting upward their orbital energies by the value G .

a figure showing $F[n]$ as a function of $\lambda \in [0, 1]$, for Ne^{6+} , will not allow the eye to see any difference between the curves produced when keeping the density constant or by following the proposal of Harris and Jones [69], where the external potential is approximated by a linear combination of the limiting ones: $(1-\lambda)V(\lambda=0) + \lambda V(\lambda=1)$ (cf. [58]). This happens despite the near-degeneracy effect present in this system, which is not seen at the noninteracting point $\lambda = 0$.^{*} Thus, it seems that there are ways to define $V(\xi)$ to keep the changes in density (and those in the energy associated with it) within reasonable limits.

Thus, the Hamiltonians will be ξ -dependent, having the form

$$H(\xi) = H_0(\xi) + V(\xi),$$

where $H_0(\xi)$ has nonlocal one-particle operators and/or two-particle operators, while $V(\xi)$ is a local potential operator.

Figure 8 shows an example of the evolution of $F[n]$, as a function of ξ , while keeping n constant for two different choices of ξ , one coming from $r_{12} \rightarrow \lambda/r_{12}$, $\lambda = \xi$, and the other from $r_{12} \rightarrow \text{erf}(\mu r_{12})/r_{12}$, $\mu = \xi/(1-\xi)$.

Although it is tacitly assumed that the nature of the ground state is conserved along the adiabatic connection, there is no guarantee for it. We know that the degree of degeneracy can change along with ξ . We cannot exclude the possibility of state crossings along this connection (see, e.g., [74, 75]). If a crossing occurs we can either follow the state or change to the new ground state, following the philosophy of the HK theorem.

^{*}The Harris–Jones adiabatic connection not only has the same end-points as the one keeping the density constant but also the derivative at the end-points [60]: The curve showing the dependence of $F_\lambda[n]$ on λ is well fitted with four parameters.

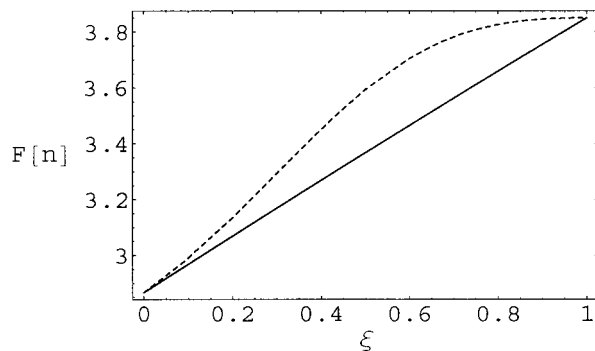


FIGURE 8. $F[n]$, as a function of ξ , where n is the ground-state density of the He atom (a.u.). Interaction between particles ξ/r_{12} (full curve) or $\text{erf}[\mu r_{12}\xi/(1-\xi)]/r_{12}$ (broken curve). The data are provided by accurate calculations of the He atom [60, 62].

The effect of the parameter-dependent external potential on the appearance of crossings has not been studied. Keeping the density constant seems to have the effect of helping to avoid the crossings.

Let us transform the parameter of the adiabatic coupling such that $\xi \in [0, 1]$, $\xi = 0$ defining a noninteracting system and $\xi = 1$ the physical one. The functionals pertaining to the model system will be indexed by ξ , e.g., $F_\xi[n]$; we will omit the index when $\xi = 1$. Introducing the notation $\bar{F}_\xi[n] = F[n] - F_\xi[n]$, we have

$$E[n, \nu] = F[n] + \int n\nu = F_\xi[n] + \int n\nu + \bar{F}_\xi[n]. \quad (7)$$

To get the ground-state energy, we have to require $\delta E[n, \nu] = 0$. We have thus to treat a system described by a Hamiltonian having two-particle and/or nonlocal one-particle operators implicit in $F_\xi[n]$ in an external potential given by $\nu_\xi(r) = \nu(r) + \delta \bar{F}_\xi[n]/\delta n(r)$. We thus see that $\bar{F}_\xi[n]$ has a double role: first, to yield a correction to the model calculation to yield the physical ground-state energy; second, to yield the potential that guarantees that the density of the model system is the same as the ground-state density of the physical system.

The idea behind the approach just presented is to make a computation for a reference, model system, at a given ξ , by using a wave function method, and use approximations for the universal density functional $\bar{F}_\xi[n]$. Of course, such an approach relies totally upon the feasibility of the calculation of $F_\xi[n]$

+ $\int n\nu$ and upon the chance of finding good approximations for $\bar{F}_\xi[n]$.

As long as ξ stays small, we can expect to have a model that is simple to treat. For example, when operators like λ/r_{12} or $\text{erf}(\mu r_{12})/r_{12}$ are used at $\lambda = 0$ (or $\mu = 0$) only an independent-particle model has to be solved.

The complexity of the model does not increase fast with ξ . Figure 9 shows, for the He atom, the evolution of the error in the energy by limiting the wave function to one configuration ($1s^2$), two configurations ($1s^2, 2s^2$), or three configurations ($1s^2, 2s^2, 2p^2$) as λ varies between 0 and 1. Setting an acceptable energy error value to a given threshold (say, 1 mhartree) one can go up to a given λ ($\lambda_1 \approx 0.15$ for He). Deciding to go further with λ , while keeping the same accuracy, requires at least a two-configuration calculation. In the case of He, λ can stay below $\lambda_2 \approx 0.2$. Note that when increasing λ beyond a certain limit quickly requires including more and more configurations. When near degeneracy is present, the point where one needs to give up the monodeterminantal wave function gets closer to the origin. For example, in the Be atom we obtain for this point $\lambda_1 \approx 0.09$, while for Ne^{8+} , where the near-degeneracy effect is stronger, λ_1 is decreased to $\lambda_1 \approx 0.06$. This does not occur in the He series, where no near-degeneracy effect is present; for Ne^{8+} , λ_1 has a value close to that for He.

A similar behavior should be present for all choices of the adiabatic connection. It might happen, however, that one choice gives smaller errors for a larger domain of ξ than the other. First, this definition has to be made more specific, as we have

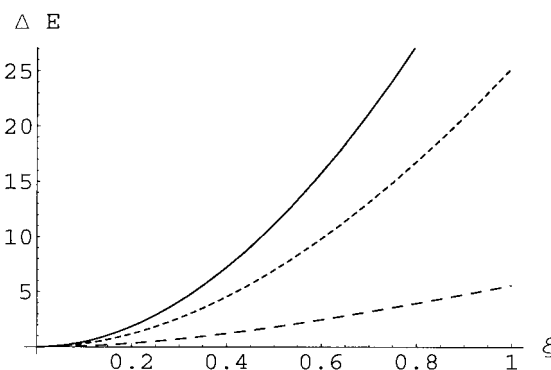


FIGURE 9. Difference between the accurately computed $F_\xi[n] + \int n\nu$ and $\langle \Psi' | H(\xi) | \Psi' \rangle$, where Ψ' is limited to one ($1s^2$) two ($1s^2, 2s^2$), or three ($1s^2, 2s^2, 2p^2$) configurations (full, dotted, or broken curves, respectively) for the He atom (mhartree) from an accurate calculation [60].

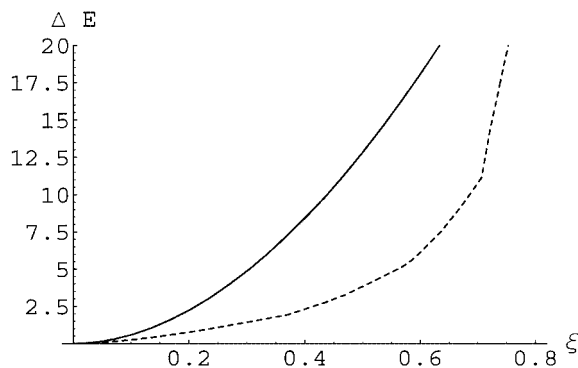


FIGURE 10. Error made by using a two-configuration wave function in Be as a function of ξ . The full line shows the results for $\xi = \lambda$, when λ/r_{12} replaces $1/r_{12}$, while keeping the density constant. The broken line shows the results for $\text{erf}(\mu r_{12})/r_{12}$ by choosing μ in such a way that the expectation value of the single determinant wave function is the same for $H(\lambda)$ and $H(\mu)$.

to choose how we can compare, say, λ/r_{12} with $\text{erf}(\mu r_{12})/r_{12}$. One possible approach is to choose a dependence between, in our example, λ and μ by considering them equivalent if $\langle \Phi | H(\lambda) | \Phi \rangle = \langle \Phi | H(\mu) | \Phi \rangle$, where Φ is the optimized single determinant wave function.

Figure 10 shows such a comparison for error made by using a two-configuration approximation to the wave function for Be.

We have seen above that we started with a model system and transformed it continuously into the physical one. Evidently, one can gather information on several points along this path (or on different points on different paths) and try to extrapolate to the physical system (cf. [76, 77]). In fact, one can see the construction of the $\bar{F}_\xi[n]$ as a clever technique of extrapolation. One can, however, imagine model systems that are beyond the physical system and use interpolation techniques. For example, one can imagine, with λ/r_{12} , to let $\lambda \rightarrow \infty$, which produces systems analogous to the Wigner crystal [78].

The next step, to be discussed below, will be that of choosing an approximation for $\bar{F}_\xi[n]$. When $\xi \rightarrow 1$, $\bar{F}_\xi[n] \rightarrow 0$. However, the effort of the calculation will be equivalent to that of a standard wave function method. A compromise has to be found, and this is dependent on the quality of the approximation one can find for $\bar{F}_\xi[n]$.

Before treating this subject we will consider in more detail the case when $\xi = 0$, which is the standard KS method.

KS Method

When no degeneracy is present in the noninteracting system, $F_{\xi=\lambda=0}[n] = T_s[n] = \min_{\Psi \rightarrow n} \langle \Psi | T | \Psi \rangle$ (cf. [63]), and the problem of finding the ground state of the system with external potential ν is transformed into that of

$$\min_n \min_{\Psi \rightarrow n} \langle \Psi | T | \Psi \rangle + \int n\nu + \bar{F}_{\lambda=0}[n] \quad (8)$$

or

$$\min_{\Psi} \langle \Psi | T | \Psi \rangle + \int n_{\Psi} \nu + \bar{F}_{\lambda=0}[n_{\Psi}], \quad (9)$$

where n_{Ψ} means that n is constructed from Ψ . As T is a one-body operator, as is $V_{\text{KS}} = \sum_{i=1, N} \nu_{\text{KS}}(r_i)$, with $\nu_{\text{KS}}(r) = \nu(r) + \delta \bar{F}_{\lambda=0}[n] / \delta n(r)$, a minimizing Ψ is a Slater determinant (the KS determinant Φ_{KS}).^{*} Together with the orthogonality condition for the orbitals in Φ_{KS} , this yields a Schrödinger equation (the KS equation) for the independent-particle (KS) Hamiltonian $T + V_{\text{KS}}$. The KS method thus requires finding the KS orbitals, eigenfunctions of the KS Hamiltonian. They yield the exact density of the system with N electrons in the external potential ν .

Finding the Hamiltonian of the KS system, in other words the potential of a system of “noninteracting electrons,” yielding a given density, has been often done numerically (see, e.g., [31]). The understanding of the behavior of these potentials has been useful for the design of new approximate density functionals (see, e.g., [79, 80]).

In the case of degeneracy of the KS system, one might be forced to use an ensemble (to consider several of the degenerate KS determinants) to obtain the given density n . The previous line of thought is repeated by using instead of $T_s[n_{\Phi_{\text{KS}}}]$

$$T_s[n] = \sum_i w_i T[n_i], \quad (10)$$

where the n_i are built from the degenerate KS determinants and w_i is chosen such that $n = \sum_i w_i n_i$, with $\sum_i w_i = 1$ (see, e.g., [81]).

^{*}One can see V_{KS} as the potential that forces independent fermions to have a ground-state density n .

One may ask whether we always have a ground-state wave function yielding a given density n . The question may be reformulated as: “Can one find a suitable potential such that the corresponding ground-state wave function yields the given density n ?” If the answer is “yes,” the density is called *pure-state ν -representable*.

For the real system, the problem is not posed as the potential is known anyhow. When performing KS calculations, one has to ask about the existence of a potential for a system of noninteracting particles yielding a given density, the KS potential, ν_{KS} .

However, examples show that the density is not always noninteracting pure-state ν -representable. They are in general based on the following construction [51, 64]. Consider a given potential that presents degeneracy for a system of N particles, none of the states yielding a totally symmetrical density. Construct the equiensemble density of this system, which is totally symmetrical. We thus have a density that is not produced by any of the eigenstates of the Hamiltonian with the given potential. Consider just a simplified example of independent particles in a spherical box. The ordering of levels is $1s, 1p, \dots$ for $N \in [3, 7]$. For $N = 3$, we have an equiensemble density that is spherically symmetrical. The density obtained by occupying one of the p spin orbitals contains a component with angular momentum $l = 2$ and thus is not totally symmetrical. One can imagine now to relax the spin orbitals, so that they are not spin eigenfunction any more. The $p_{1/2}$ orbital is spherically symmetrical, but with increasing N we will be forced to occupy $p_{3/2}$, which is not.

Imagine now that we go the opposite way: We know the density and ask about a potential that yields this equiensemble density. Take $N = 4$. If we insist in occupying $1s$ and the $2s$ orbitals, we may obtain such a potential. However, we will find p states that lie below the second s state: The density obtained is not that of a ground-state density.

One may go a step further and ask whether one can find a suitable potential such that a corresponding ground-state ensemble density is equal to a given density n (*ensemble ν -representability*). To the best of our knowledge, there is no general proof for it, but no relevant counterexample is known. (See, however, Refs. [82, 83] for more detailed discussions.) The particle in a spherical box, the harmonic oscillator, or the system having the hydrogenic density for $N = 4$ are examples that are not pure state but ensemble ν -representable, as the p orbitals are

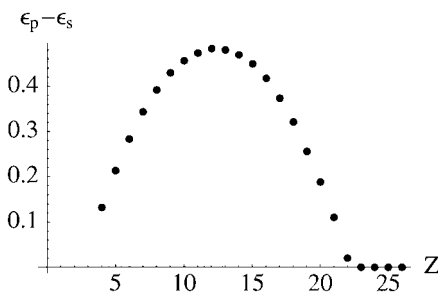


FIGURE 11. Difference between the $2p$ and $2s$ KS orbital energies, in the Be series, as a function of the nuclear charge Z (hartree) from accurate calculations.

occupied before the $2s$ ones (the harmonic oscillator) [60, 84].

We know that for Hartree–Fock relaxing all constraints ensures that the determinant built from the orbitals having the lowest eigenvalues of the Fock operator yields the lowest expectation value of the Hamiltonian [85]. Interestingly, such a proof seemingly contradicts numerical experience, as one notes in practice inversion of the ordering of levels. This is, of course, due to restrictions imposed onto the one-particle eigenfunctions in practically all programs used.

An equivalent theorem is not proven in KS theory, although it touches the foundation of the procedure while in Hartree–Fock it does not: Hartree–Fock requires that the wave function minimizes $\langle H \rangle$, while KS theory requires that the KS solution is the ground state of a system of independent particles. The absence of a ground-state ensemble of noninteracting particles yielding the given density would mean that the KS model cannot be applied.

It seems natural to expect that the KS system presents degeneracy (and thus opens the problem of the ensemble treatment) when the physical system presents degeneracy. However, it has been noted both in accurate (cf. [86]) and in approximate KS calculations (see, e.g., [87] or [88]) that the KS system may present degeneracy even when the physical system does not. Such cases are not uncommon [89]. This is usually related to near-degeneracy effects, as it appears, e.g., for the C_2 molecule [86]. It is absent, however, in the H_2 molecule even at larger interatomic distances [90].

In Figure 11, we show the difference between the $2p$ and $2s$ KS orbital energies (obtained from accurate calculations [60]) in the Be series. Note that for the ions with nuclear charge $Z < 23$ the points seem to lie on a parabola that cuts the axis; the KS state has $1s^2 2s^2$ occupation. Above $Z = 23$, the KS $2s$ and

$2p$ states remain degenerate. To get the ground-state density of the ion (which is in the nondegenerate 1S state) we have to assume an occupation $1s^2 2s^{2-x} 2p^x$, where x slowly increases from x close to 0 at $Z = 23$, to $x \approx 0.1$, for $Z \rightarrow \infty$ (cf. [91]).

Another peculiarity of KS potentials is that they can be different for densities that are produced by degenerate states of the same physical potential: There is no reason to expect, in general, that a density that is not totally symmetrical is produced by a KS potential that is. An analytic example can be found in [92], where this aspect is discussed in detail.

The shape of the KS potential may have some peculiar features (see, e.g., [93, 94]). One of them that is largely unexplored is the possibility to find jumps in it (see, e.g., [93]). Consider, for example, a Rb and a He atom at large internuclear separation. No charge transfer takes place, as the electron affinity of an atom is smaller than the ionization potential of the other, in contrast to the situation of $\text{He}^+ \cdots \text{H}$, discussed above. The densities are essentially those of the isolated atoms. Consider now the corresponding KS system. As the densities are practically unchanged, the KS potentials around each of the atoms are also expected not to change. From accurate calculations (see, e.g., [95]), we know that the $2s$ orbital energy of the He KS system is of ≈ 4.3 eV for a KS potential approaching 0 asymptotically. The KS system giving the He atom density has a positive electron affinity (which is different, of course, from the exact electron affinity of the He atom, 0). The highest occupied KS orbital energy of the Rb atom is equal to minus its ionization energy (see, e.g., [96–98]), which is ≈ 4.2 eV for a KS potential approaching 0 asymptotically. Thus, in the KS system of noninteracting particles a transfer of one electron from Rb to He brings an energy gain of ≈ 0.1 eV. This now induces a modification of the ground-state density showing that the potential considered cannot be the ground state of the $\text{He} \cdots \text{Rb}$ system considered. This seems now to be in contradiction with the Hohenberg–Kohn theorem stating that the correspondence between the density and the potential producing it is unique. Note that we assumed that the potentials of the atoms are not shifted one with respect to the other. Remember, however, that the Hohenberg–Kohn theorem fixes the potential only up to a constant. Thus, if the potential of He is shifted upward by ≈ 0.1 eV the electron density around the He atom is not changed but the electron transfer does not occur and the paradox is eliminated. Thus, the potential of the

$\text{He} \cdots \text{Rb}$ system might look like the plot shown in Figure 4, which also shows a peak in the region separating the two “atoms.” Such peaks appear also between atomic shells and are discussed in detail, e.g., in [99].

Let us consider the dissociation of a negatively charged symmetrical cluster of hydrogen atoms. As mentioned in the appendix, the equivalence of the protons produces a density of an ensemble of hydrogen atoms and negative hydrogen ions. A simple example is the dissociation of H_2^- , which produces around each of the nuclei a density that is half that of H and half of that of H^- . As, by symmetry, all atoms are equivalent, we might first not expect jumps in the potential. However, the difference between the different systems (neutral and negative ions) is still present and is visible by a division into an inner and an outer region (see, e.g., [93, 100] or [101]). Take a small excess of negative charge. In the outer regions of the atom the density is dominated by that of the negative ion, while in the inner region it is still essentially that of the neutral atom. The KS potential should look inside like that of the H atom, while outside it is that of the negative ion. As mentioned above, the ionization potential of the system is related to the tail of the density (see, e.g., [102, 103] or [98]), in our case the electron affinity of H (≈ 0.8 eV). How can that be if the potential is essentially that of the hydrogen, which has an ionization potential of ≈ 13.6 eV? We can again resolve the contradiction by shifting the potential in the inner region by $\approx 13.6 - 0.8$ eV, cf. Figure 12.

As it is well known that often parts of a molecule act chemically as if they were independent fragments it would be thus no surprise to find jumps like those shown in Figure 12 also inside molecules (cf. [105]).

NATURE OF THE COMPLEMENT FUNCTIONAL $\bar{F}_\xi[n]$

The fact that the dependence on ν can be so neatly cut off from $E[n, \nu]$ is essential for constructing approximations for $E[\nu, n]$: One simply has to concentrate on $F[n]$. We have seen that part of the problem can be eliminated by introducing a model system, which can be calculated with reasonable effort. The important question remains the approximation of the correction needed to obtain the exact energy and density, $\bar{F}_\xi[n]$.

To get more insight into the nature of $\bar{F}_\xi[n]$, let us suppose that we can continuously follow the

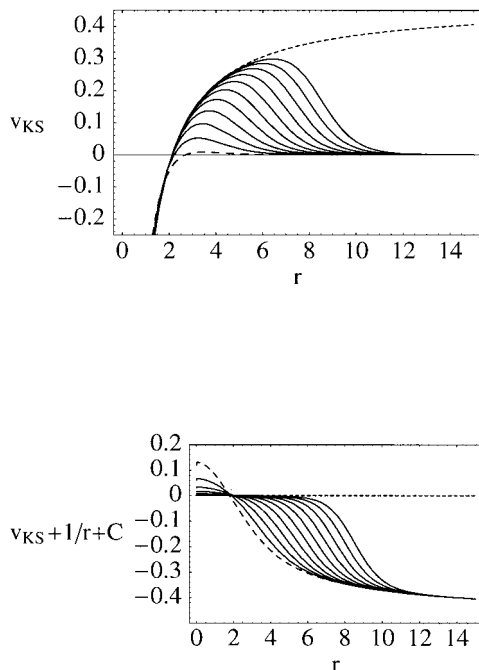


FIGURE 12. Top: KS potential of an ensemble of H and H^- and that of a hydrogen atom ($-1/r$) as a function of the radial distance r (a.u.). $w = 0$ corresponds to H, shifted upward by a constant equal to the difference between the ionization potential and the electron affinity of H ($-1/r + 1/2 - 0.0278$), short broken curve; $w = 1$ corresponds to H^- (long-broken curve). The other curves correspond to $w = 1/2, 1/2^2, \dots, 1/2^{10}$. Bottom: Difference between the KS potential and the shifted H atom potential as a function of r . The curves were obtained from accurate densities [104].

change from the model system to the physical one. Then, one can use the Hellmann–Feynman theorem (or first-order perturbation theory), which gives [70, 71]

$$\frac{d}{d\xi} E(\xi) = \left\langle \Psi_\xi \left| \frac{d}{d\xi} H(\xi) \right| \Psi_\xi \right\rangle \quad (11)$$

or, in integral form,

$$E = E(\xi) + \int_\xi^1 d\xi \left\langle \Psi_\xi \left| \frac{d}{d\xi} H(\xi) \right| \Psi_\xi \right\rangle, \quad (12)$$

where the specification $\xi = 1$ has been left out.

Note that if the density is kept constant along this process an explicit expression for $\bar{F}_\xi[n]$ is obtained after some algebra [70, 71]:

$$(\bar{F}_\xi[n]) = \int_\xi^1 d\xi \left\langle \Psi_\xi \left| \frac{d}{d\xi} H_0(\xi) \right| \Psi_\xi \right\rangle. \quad (13)$$

The integral on the right side represents the correction to be added to E_ξ to obtain the physical energy. Note that no explicit reference to the external potential $V(\xi)$ is made in the last formula: $H(\xi)$ has been replaced by $H_0(\xi) = H(\xi) - V(\xi)$. However, Ψ_ξ is required to yield n , which is guaranteed by $V(\xi)$.

If the ξ dependence in $H_0(\xi)$ is a two-body operator, e.g., λ/r_{12} (with $\xi = \lambda$), we get, for example, an explicit expression for

$$\bar{F}_{\lambda=0}[n] = \int_0^1 d\lambda \frac{1}{2} \int P_2(r_1, r_2; \lambda) / r_{12} d^3 r_1 d^3 r_2, \quad (14)$$

where $P_2(r_1, r_2; \lambda)$ is the second-order reduced density matrix, normalized to $N(N-1)$, obtained from the ground-state wave function Ψ_λ of $H(\lambda)$. This expression seems to give us $\bar{F}_{\lambda=0}[n]$. Although an equality, remember that:

1. This expressions requires the knowledge of all the $P_2(r_1, r_2; \lambda)$ for λ between 0 and 1.
2. There are infinitely many ways to connect the model system with the physical one.

Concerning the first point, remember that to obtain the exact $P_2(r_1, r_2; \lambda)$ no exact method is known, except by using the exact Ψ_λ . But, if we know $\Psi_{\lambda=1}$, our problem is already solved and there is no need for DFT. Thus, the expression showing the λ -integration cannot be used except as a motivation to construct models for $\bar{F}_{\lambda=0}[n]$.

As to the second point, we can choose, for example, instead of λ/r_{12} the connection via $\text{erf}(\mu r_{12})/r_{12}$. In that case,

$$\begin{aligned} \bar{F}_{\mu=0}[n] = & \int_0^\infty d\mu \frac{1}{2} \int P_2(r_1, r_2; \mu) \\ & \times (2/\sqrt{\pi}) \exp(-\mu^2 r^2) d^3 r_1 d^3 r_2 \end{aligned} \quad (15)$$

(see, e.g., [106]). If we use a ξ -dependent one-body operator, we may express $\bar{F}_{\xi=0}[n]$ by using only the reduced first-order density matrix, $\gamma(\mathbf{r}, \mathbf{r}'; \xi)$. For example, if we add $G\mathcal{P}$ to the Hamiltonian, where \mathcal{P} is the operator projecting out all states that are not occupied in the KS system, it comes out to be

[107] $\bar{F}_{\xi \rightarrow 0}[n] = -\int_0^\infty dG \sum_{i>N} v_{ii}(G)$, where $v_{ii}(G) = \langle \varphi_i(G) | \gamma | \varphi_i(G) \rangle$.

A simplification of $\bar{F}[n]$ may come by extracting some parts from it that are neatly defined and easily calculated. A component of $\bar{F}[n]$ is known exactly: the Hartree term (describing the electrostatic interaction of the density)

$$U[n] = \frac{1}{2} \int n(r_1)n(r_2)/|r_1 - r_2| d^3r_1 d^3r_2. \quad (16)$$

There are good reasons for computing this term exactly (cf. [41]). First, it is computationally accessible, many techniques having been developed for obtaining it with sufficient accuracy. Second, approximations (like those discussed below for the remaining part of $F_\xi[n]$) have not shown the necessary accuracy. Last, but not least, errors in the electrostatic interaction may produce catastrophic results, e.g., in ionic crystals, or as it is known from semiempirical methods in molecular calculations. As the rest of the electrostatic interaction (between nuclei and between nuclei and electrons) is treated exactly, the only source of errors would be in $U[n]$.

A problem appears for ensembles. While $\int n\nu$ is linear in n , and thus poses no problems, is not easy to construct approximations to $F[n]$ that satisfy $E[N_A, \nu] = \sum_i w_i E[N_{A,i}, \nu_A]$. There are spurious terms in $U[n]$ that have to be compensated by an unknown form of $F[n] - U[n]$: $U[\omega n_A + (1 - \omega)n_B] \neq (\omega U[n_A] + (1 - \omega)U[n_B])$ (see, e.g., [91, 108–110]). Note that the expression of the energy of the ensemble suggests that we also can use functionals depending on the densities of each member of the ensemble (by writing for each of the members $F[n_i] + \int m_i$) [91, 110]. With such an ansatz the problem mentioned above does not appear.

Once $U[n]$ is eliminated from $F[n]$, to obtain $E[\nu, n]$, only the so-called exchange correlation energy

$$E_{xc}[n] = F[n] - (T_s[n] + U[n]) \quad (17)$$

remains to be known.

Kohn and Sham [42] suggested another variant in which one takes advantage of the fact that the KS determinant is already known. The expectation value of the physical Hamiltonian, computed with the ground-state wave function of the noninteracting system, is taken away from $F[n]$; one has to approximate only the remaining part, the “correlation” energy. The exchange energy is defined as

$$E_x[n] = \langle \Phi_{KS} | V_{ee} | \Phi_{KS} \rangle - U[n] \quad (18)$$

while the correlation energy is simply

$$E_c[n] = E_{xc}[n] - E_x[n] \quad (19)$$

For $\delta E_{xc}/\delta n(r)$ (or $\delta E_c/\delta n(r)$) the terms exchange correlation (or correlation potential) are used. As the discussion for $E_{xc}[n]$ and $E_c[n]$ is often similar, we will use the notation $E_{(xc)}[n]$ for any of the two.

One should be careful about the meaning of “exact exchange” in DFT. In quantum chemistry, one is accustomed to consider as the exact exchange $E_x[\Phi] = \langle \Phi | V_{ee} | \Phi \rangle - U[n_\Phi]$, with the Slater determinant Φ being the Hartree–Fock wave function, Φ_{HF} , and n_Φ the density constructed from it. In the KS method, however, one naturally chooses as a single determinant Φ the eigenfunction of the noninteracting system, Φ_{KS} , the KS determinant. The KS determinant is not equal to the Hartree–Fock one (with a few exceptions, like the uniform electron gas, or one-electron systems): Unlike Φ_{HF} , it yields the exact n . Thus, in general, $E_x[\Phi_{KS}] \neq E_x[\Phi_{HF}]$. In analogy with the KS potential, which is local, and due to the fact that Φ_{KS} (or the exact density) is not a priori known, one can generate an “optimized effective potential” (OEP), optimized in the sense that it is the local potential that produces for the noninteracting Hamiltonian the eigenfunction, Φ_{OEP} , having the lowest expectation value of the physical Hamiltonian. (Remember that the Hartree–Fock method yields the determinant giving its lowest value; we thus have: $\langle \Phi_{HF} | H | \Phi_{HF} \rangle \leq \langle \Phi_{OEP} | H | \Phi_{OEP} \rangle \leq \langle \Phi_{KS} | H | \Phi_{KS} \rangle$). Further, approximations to Φ_{OEP} exist, like the Krieger–Li–Iafrate method, KLI, which produce further determinants, and thus further definitions of exchange. It turns out that—when no degeneracy is present—all these wave functions are similar, and the values of exchange energy are close, too (see, e.g., [111]).

Of course, there is a definition of “exact correlation” that goes along with each definition of exact exchange. Using $\langle \Phi_{HF} | H | \Phi_{HF} \rangle \leq \langle \Phi_{KS} | H | \Phi_{KS} \rangle$, or $E[n(\Phi_{HF}), \nu] \geq E[n_\nu, \nu]$, relationships can be derived between the various definitions of E_c [112–114]. For the correlation energy, one seems to notice larger discrepancies when near degeneracy is present: We estimate the difference between the DF and usual quantum chemistry definition to 2 mhartree for Be and to 12 mhartree for Ne^{6+} [60, 115].

Of course, $E_{(xc)}[n]$ can be defined in a similar way along the adiabatic connection for $\xi \neq 0$. In this

case, one should also treat the Hartree term correctly, and thus extract it from $\bar{F}_\xi[n]$, remembering that part of it, $U_\xi[n]$, has been treated within $F_\xi[n]^*$:

$$E_{xc,\xi}[n] = \bar{F}_\xi[n] - (U[n] - U_\xi[n]) \quad (20)$$

and

$$E_{c,\xi}[n] = \bar{F}_\xi[n] - (\langle \Phi_{KS} | H_0 | \Phi_{KS} \rangle - \langle \Phi_{KS} | H_0(\xi) \rangle). \quad (21)$$

Of course, other reference systems than the KS one are possible. In the last decade, the OEP has gained in popularity, also in connection with its simplified form, the KLI potential (see, e.g., [116]), or more recent extensions in Refs. [117, 118]. Usually, such approaches are considered still as a part of DFT, one of the arguments being the fact that these potentials are local, which can be corrected by other, approximate, weaker (“correlation”) potentials to give the KS potential and thus the exact density.

PROPERTIES

The KS system has been described above as fictitious, as it corresponds to nonexisting, noninteracting particles. It turns out, however, that it can often produce information that is physically significant, being close to the one that would be obtained from the exact wave function. Evidently, any expectation value of a local one-particle operator is correct, as the density coming out from KS is exact. For example, molecular dipole moments are exact when no approximations are made for the KS potential, and so are polarizabilities. Less evident is the property mentioned above: that the highest KS eigenvalue is equal to minus the ionization potential (see, e.g., [102], [103], [96], or [98]).

One may, however, use the KS wave function with success beyond its rigorous limits. One may deduce reasonably good values for excitation energies (cf., e.g., [95]) or vertical ionization potentials [119]. Arguments have been given that KS orbitals should be close to Dyson orbitals (see, e.g., [120]). Last but not least, the KS wave function respects the Pauli principle, which is essential to understand the variety of chemistry: It is a useful tool for interpretation (see, e.g., [16]).

*Note that some confusion may arise with this notation, as often $E_{(x)c,\xi}$ is used as a notation for the exchange and/or correlation energy of the system with $H(\xi)$.

Much experience comes from approximate calculations. An example is the total spin angular momentum. As S^2 is a two-body operator, the KS determinant should not be expected to give a reliable value for it [121]. Nevertheless, it is used in approximate DF calculations; there is experience that shows that its expectation value can be more reliable than that obtained in unrestricted Hartree–Fock calculations [122, 123].

Note in this category the success of DFT for describing properties derived from NMR or ESR spectra (see, e.g., [124]).

There are rigorous ways to obtain properties within DFT. However, the knowledge of property-dependent functionals is required.

A way to obtain the properties by keeping the DFT philosophy is to find an operator conjugate to the property. The typical example is the excess of spin-up over spin-down density, $m(r) = n_\uparrow(r) - n_\downarrow(r)$. For it a nonuniform magnetic field is introduced into the Hamiltonian, which couples only to m , and does not modify the kinetic energy operator ([42, 125]; see also [126, 127]). This approach has been later generalized [128]. It consists of observing that the trick of defining $F[n] = \min_{\Psi \rightarrow n} \langle \Psi | T + V_{ee} | \Psi \rangle$ can be applied on $F[n]$, too, to get $F[n, m] = \min_{\Psi \rightarrow n, m} \langle \Psi | T + V_{ee} | \Psi \rangle$, which can be obtained by considering a field coupled to m (like v was coupled to n) to obtain $F[n, m]$. Once $F[n, m]$ is known, one can use $E[n, v] = \min_{n, m} F[n, m] + \int v m = \min_{\Psi} \langle \Psi | T + V + V_{ee} | \Psi \rangle$, which automatically yields m associated with the ground state. Of course, the next step is to define $F[n, m]$ for modified Hamiltonians and define a corresponding KS method. In it,

$$\begin{aligned} T_s[n] &\rightarrow T_s[n_\uparrow, n_\downarrow] = \min_{\Psi \rightarrow n, m} \langle \Psi | T | \Psi \rangle \\ &= \sum_{i=1, N_\uparrow} \left\langle \varphi_i \left| -\frac{1}{2} \nabla^2 \right| \varphi_i \right\rangle + \sum_{i=1, N_\downarrow} \left\langle \varphi_i \left| -\frac{1}{2} \nabla^2 \right| \varphi_i \right\rangle, \quad (22) \end{aligned}$$

where $N_\uparrow = \int n_\uparrow$ and $N_\downarrow = \int n_\downarrow$. Further, $E_{xc}[n] \rightarrow E_{xc}[n_\uparrow, n_\downarrow]$. (Note that we are free to replace the dependence on n, m by that on n_\uparrow, n_\downarrow .)

Similar in spirit is the use of response theory within DFT. Excitation energies can be obtained in time-dependent DFT by studying the change of the density produced by a time-dependent perturbing potential: The perturbation couples the ground to the excited states and the time or frequency dependence is the tool exploring it (see, e.g., [129, 130]).

Another procedure to obtain properties from DF calculations was first proposed for momentum distributions [131] and then generalized to arbitrary properties [132]. The main idea is to add to the Hamiltonian the operator corresponding to the property in which we are interested, \hat{O} , multiplied by a vanishingly small constant η . The universal functional becomes now dependent on \hat{O} and η . Next, the Hellmann–Feynman theorem is applied, yielding a correction to the expectation value of \hat{O} calculated for the noninteracting (model, KS) system, which is equal to the derivative of the $E_{xc}[n]$ with respect to η .

It is evident that for a mathematically rigorous theory many details have to be clarified in these approaches. To give just one example: Can we always obtain that we generate a given property with the wave function we are using in the search? We know, for example, that the on-top pair density $P_2(r, r)$ can take values, for an approximate multi-determinant wave function, that are not reproducible by a $P_2(r, r)$ coming from a single Slater determinant [133]. To our knowledge, such a problem has not been found when replacing the approximate by the exact wave function, which is no proof, of course, that the problem does not appear. Another question is: Do the properties we obtain really have the meaning we attribute to them? For example: Are the spin densities in approximate DFT really spin densities or do they reflect a different property? (see, e.g., [134] or [135]).

Approximate Exchange and Correlation Functionals

NEED FOR APPROXIMATIONS

The KS approach tells us that we have only to treat a model system if we know a density functional $\bar{F}_\xi[n]$ (or $E_{xc,\xi}[n]$ or $E_{c,\xi}[n]$). However, these functionals remain unknown, and there is not much hope of getting them to arbitrary accuracy without performing a many-body calculation. Once the latter is done, the functionals can be obtained, of course, but this is only of interest for analyzing the functionals.* Thus, DFT has no procedure similar to that of many-body theory, where the wave function can be improved systematically and the limit is

*Note, however, that there is some hope that keeping the density constant (or using local potentials) in many-body calculations might be a better way to tackle the many-body problem (see, e.g., [72, 73, 136–138]).

imposed only by the performance of the computer. In DFT, approximations are constructed for $\bar{F}_\xi[n]$, and it is believed that the ingenuity of researchers can allow finding better and better approximations for it.

The adiabatic connection provides what one might call a systematic improvement, as one approaches the exact solution, as ξ gets closer to 1. Although $\bar{F}_\xi[n]$ remains unknown, its importance decreases with increasing ξ . It is our hope that the connection may be chosen in a way to improve the ability to approximate $\bar{F}_\xi[n]$ beyond a given ξ , say, ξ_0 , which should be sufficiently small to calculate Ψ_ξ with reasonable computational cost. For $\xi > \xi_0$, the results should not change within a given numerical accuracy.

There are essentially two strategies to construct the density functionals:

1. Use exact conditions to be satisfied by $\bar{F}_\xi[n]$.
2. Fix the functional so that it reproduces some data.

Some of the exact conditions can be found, e.g., in [139]. The problem of using exact conditions is that we know only the necessary, but not the sufficient, conditions: One can satisfy many conditions but violate one important, unknown condition [45]. In the last decade there was a strong tendency to fit to experimental data, arguing that we know that the functional exists and that the way to get it does not matter. The problem with fitting to data is that the parameters can fit one class of systems or properties but not another. In practice, both approaches are present in the construction of functionals, putting more emphasis onto the first, or second, strategy.

(SEMI-)LOCAL APPROXIMATIONS

Usually the approximation is made by choosing an ansatz for the functional. The simplest one gives rise to the so-called local density approximation (LDA):

$$E_{(x)c}[n] \approx \int n(r)\varepsilon_{(x)c}(n(r))d^3r. \quad (23)$$

It is usually considered that this should reproduce the uniform electron gas result. In the uniform electron gas, n does not depend on r , so that $\varepsilon_{xc}(n)$ becomes the exchange correlation energy per parti-

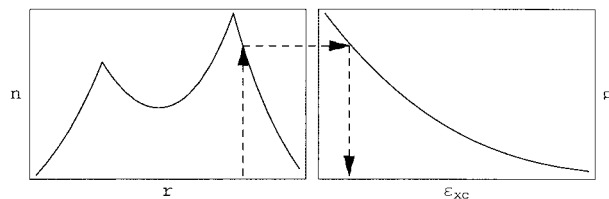


FIGURE 13. Schematic representation of the LDA approximation. For a given position r , the density n is given (left). For the same density, the exchange correlation energy per particle, ε_{xc} , of the uniform electron gas is found.

cle in the uniform electron gas. Using the “universal” character of the functional, it can be applied for every system: In each point of space $r \rightarrow n \rightarrow \varepsilon_{xc}$ (cf. Fig. 13). Of course, this is an approximation as it can be seen, e.g., by applying $E_{xc}[n]$ for the hydrogen atom: The use of ε_{xc} given by the uniform electron gas does not exactly compensate $U[n]$.

The functional derivative of the local functionals gives an approximation to the KS potential. The potential obtained in the LDA approximation fails to show several characteristics of the exact KS potential. One of them is the inability to produce the “jumps” mentioned above (see, e.g., [80]). Another is that it decays too fast (exponentially, unlike the exact KS potential, which decays in atoms and molecules like $1/r$) (cf. Fig. 14). This feature is important when trying to describe excited states and properties related to them.

The LDA can be defined also for a nonzero ξ . For λ/r_{12} there are simple scaling relationships that connect $\varepsilon_x(n; \lambda)$ and $\varepsilon_c(n; \lambda)$ with $\varepsilon_x(n; \lambda = 1)$ [140] and $\varepsilon_c(n; \lambda = 1)$ [141]. Thus, no new calculations are needed to obtain the λ -dependent values for approximating $\bar{F}_{\lambda \neq 0}$.

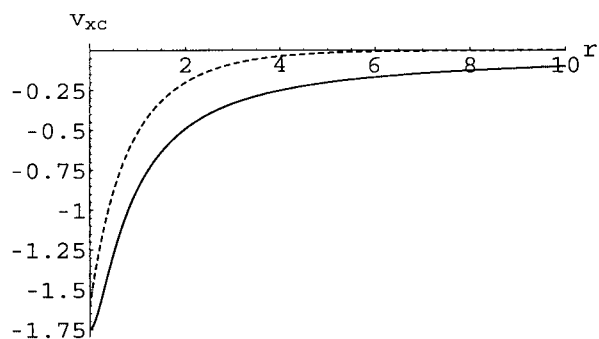


FIGURE 14. Exact (full curve) and LDA exchange correlation part of the KS potential, $\delta E_{xc}/\delta n(r)$, as a function of the radial distance for the He atom (a.u.).

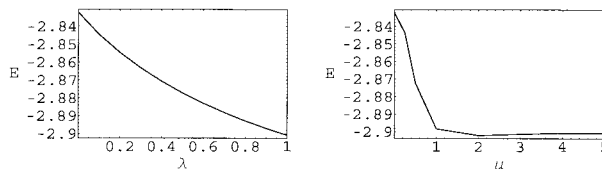


FIGURE 15. Evolution of the energy with the coupling parameter in the LDA for the He atom in two different couplings: λ/r_{12} (left) and $\text{erf}(\mu r_{12})/r_{12}$ (right) (a.u.).

For other adiabatic connections, despite some simplifications that can be introduced via scaling relationships, new data are needed. As for $\xi = 0$, they can be obtained from uniform electron gas calculations, cf. [142] or [110]. The exchange energy can be computed analytically, but the correlation energy per particle has to be computed numerically, for a set of values of μ and a set of densities, and then fitted [110]. Normally, they are monotonous functions of ξ and the density: As the density increases, so does the (exchange-)correlation energy (in absolute value), while the opposite effect happens with the increase of ξ .

The different couplings yield different results once the LDA is applied. Figure 15 shows the evolution of the energy, as a function of ξ , when the local approximation obtained from the uniform electron gas is used for the exchange and correlation part of $\bar{F}_{\xi}[n]$ for a calculation of the He atom. In the λ -coupling (λ/r_{12}) the error of the LDA slowly disappears as λ increases to 1. In the μ -coupling ($\text{erf}(\mu r_{12})/r_{12}$), the LDA suddenly drops down, becoming small as soon as $\mu \approx 1$ a.u. (comparable to a representative inverse mean distance between electrons in the He atom).

To compare the λ - with the μ -coupling, a common scale has to be chosen. As the (exchange-)correlation energy to be described by $\bar{F}_{\xi}[n]$ decreases monotonically with ξ , we plot below the errors produced by using the LDA form of the functionals as a function of the value it is aimed to produce. Figure 16 shows the plots of the LDA errors $E_{(x)c,\lambda}$ and $E_{(x)c,\mu}$ for He. The point where E_{xc} becomes better in the μ -coupling than in the λ -coupling is related to the size of the system. To understand what happens, recall that $\text{erf}(\mu r_{12})/r_{12}$ describes the long-range interaction and $E_{xc,\mu}$ has to describe the short-range part. If $1/\mu$ is larger than the size of the system, one wrongly assumes that some correlation

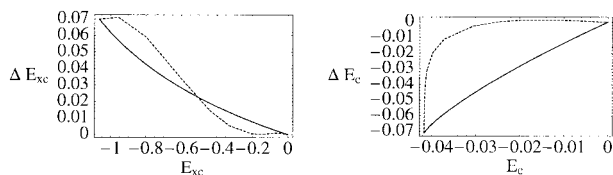


FIGURE 16. Exchange correlation energy LDA error (left) and correlation energy LDA error (right) as functions of the exact E_{xc} and E_c , respectively, along the adiabatic connection for He (a.u.). The adiabatic connection is λ/r_{12} (full curve) and $\text{erf}(\mu r_{12})/r_{12}$ (broken curve).

effects can be transferred from the uniform electron gas where the electrons are present beyond this distance. The improvement by using the μ -coupling instead of the λ -coupling is more dramatic on E_c . In both cases one notes that after a certain value of μ there is only a small error in using LDA.*

The observation on He can be put in a more general context. It has been known for a long time that the uniform electron gas presents some specific long-range correlation effects, and a way to treat it was to separate them by splitting the operator describing the interaction between electrons in a short- and long-range part [143]. [In our case this corresponds to splitting it into $\text{erfc}(\mu r_{12})/r_{12}$ and $\text{erf}(\mu r_{12})/r_{12}$.] The short-range part had been treated by standard methods (it was simply second-order perturbation theory). As a further physical argument, it is natural to expect that the role of the external potential is less important than the diverging repulsion between electrons when the latter are close to each other. One may thus expect that transferability works better for the short range. Accordingly, there were several proposals, in different contexts, to split $1/r_{12}$ into a short- and long-range part in DFT, constructing LDA or LDA-like approximations for the short range (see, e.g., [144–146]), the use of $\text{erf}(\mu r_{12})/r_{12}$ [110] being extremely convenient for the use in molecular programs using Gaussian basis sets.

Although not well known, it is also possible to choose ϵ_{xc} in local approximations to atomic data in a way to ensure that both the energy and the density produced for the atom are exact (see, e.g., [147–149]). We show in Figure 17 the plot of the LDA ϵ_{xc} obtained in the uniform electron gas and that defined in such a way that it yields the correct energy

*Of course, this does not mean that one should not use the λ -coupling: In our example, extrapolation seems easier to obtain when using the λ -coupling.

and density for the Be atom and the Ne^{6+} ion [149]. As the density is monotonically decreasing, there is a one-to-one relationship between r and $n(r)$, or $r_s = (3/4\pi n)^{1/3}$. ϵ_{xc} is shown in Figure 17 as a function of $1/r_s$ with $r_s = 3/(4\pi n)^{1/3}$, which would be a straight line in this plot for the uniform electron gas exchange-only approximation. Note for the atomic LDA the jump in ϵ_{xc} at the shell boundary, which is not present in the uniform electron gas LDA, but striking in the atomic LDA, especially for Ne^{6+} .

It is, of course, unphysical to consider that in each point of space the electrons behave as if they were in a uniform electron gas. One can think of different ways to correct it. One may introduce a dependence on the finite electron number (see, e.g., [150, 151]). The problem with this approach is extensivity: If we have two infinitely separated fragments, the energy should be the sum of that obtained for the fragments. If we compute one fragment individually, we know only the number of particles in it. If we compute the total system, we use the total number of electrons in the system.

Another way to overcome the usual LDA approximation is to realize that there is no gap in the uniform electron gas, while it is a common feature of the majority of electronic systems. One could thus introduce the dependence on a gap (see, e.g., [107, 152, 153]).

The most popular way to go beyond the LDA is the semilocal approach: to look not only at the density at r but also in its neighborhood. In other words, one can gather information by using ∇n , etc. (cf., e.g., [41, 154–158], etc.):

$$E_{(x)c}[n] \approx \int n(r)\epsilon_{(x)c}(n(r), |\nabla n(r)|)d^3r. \quad (24)$$

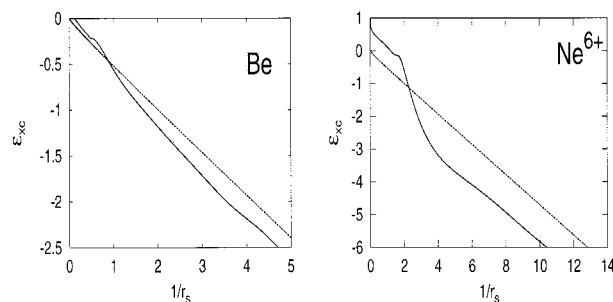


FIGURE 17. ϵ_{xc} in the LDA as a function of $1/r_s$ generated to reproduce the correct atomic energy and density (full curves) for the Be atom (left) or the Ne^{6+} ion (right) [149]. For comparison, the usual LDA, fitted to reproduce the uniform electron gas data, are also given (dotted curves) (a.u.).

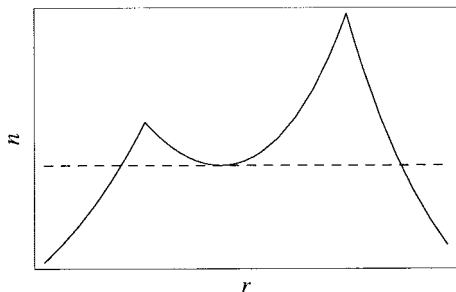


FIGURE 18. Schematic plot of the density in a molecule. The density (full curve) takes the same value (broken line) in the bonding and in the outer regions but the gradient of the density is different.

Note that only the absolute value of the gradient enters this expression due to the concern of keeping the universality of the functional (cf., e.g., [41]). With such an approach, the binding region in a molecule, where the density gradient is close to zero, yields a different contribution from that in the outer regions of the molecule having the same density (cf. Fig. 18).

An extension is (see, e.g., [159–162])

$$E_{(\text{x})c}[n] \approx \int n(r) \varepsilon_{(\text{x})c}(n(r), |\nabla n(r)|^2, \nabla^2 n(r), \tau(r)), \quad (25)$$

where $\tau(r) = \sum_{i=1,N} |\nabla \varphi_i|^2$, where φ_i are the KS orbitals. This type of approximation is now often called meta-GGA, while the form $\varepsilon_{\text{xc}}(n(r), |\nabla n(r)|)$ is referred to GGA (generalized gradient approximation).

CAN THE APPROXIMATIONS BE UNDERSTOOD?

A way to understand the nature of ε_{xc} is based upon a formula obtained from the adiabatic connection:

$$\begin{aligned} E_{\text{xc}}[n] &= \bar{F}_{\lambda=0}[n] - U[n] \\ &= \frac{1}{2} \int d^3r d^3r' \frac{1}{|r-r'|} \\ &\quad \times \int d\lambda [P_2(r, r'; \lambda) - n(r)n(r')] \\ &= \int d^3r n(r) \frac{1}{2} \int d^3r' \frac{1}{|r-r'|} \end{aligned}$$

$$\begin{aligned} &\times \int d\lambda [P_2(r, r'; \lambda)/n(r) - n(r')] \\ &= \int d^3r n(r) \frac{1}{2} \int d^3r' \frac{1}{|r-r'|} n_{\text{hole}}(r, r'). \end{aligned} \quad (26)$$

$n_{\text{hole}}(r, |r-r'|)$ is the λ average of $[P_2(r, r'; \lambda)/n(r) - n(r')]$. As exchange and correlation lower the probability to find two electrons at the same point r , $n_{\text{hole}}(r, 0) \leq 0$. The index “hole” comes from the picture that the exchange correlation energy can be viewed from the last formula as the Coulomb interaction with a position-dependent positive charge, or a hole in the density, one can decide to model. A further step is to spherically average (around r) P_{hole} and model it (see, e.g., [71, 163]). If this model is good, so will be $\frac{1}{2} \int d^3r' (1/|r-r'|) P_{\text{hole}}(r, r')$. If we use in this model only $n(r)$ and $\nabla n(r)$, this integral yields a function of these quantities, which we can identify with a form for $\varepsilon_{\text{xc}}(n(r), |\nabla n(r)|)$. An expansion of the exchange hole also introduces terms like $\nabla^2 n(r)$, or $\tau(r) = \sum_{i=1,N} |\nabla \varphi_i|^2$, where φ_i come from the series expansion of the exchange part of n_{hole} (cf. [112] or [158]).

We show in Figure 19 the plot of $\frac{1}{2} \int d^3r' (1/|r-r'|) \int d\lambda [P_2(r, r'; \lambda)/n(r) - n(r')]$ as a function of the radial distance, r , in the He atom, as obtained from an accurate calculation [164]. In the same plot, we compare it with $\varepsilon_{\text{xc}}(r)$, as given by a GGA approximation [165] that intends to model the exchange correlation hole.

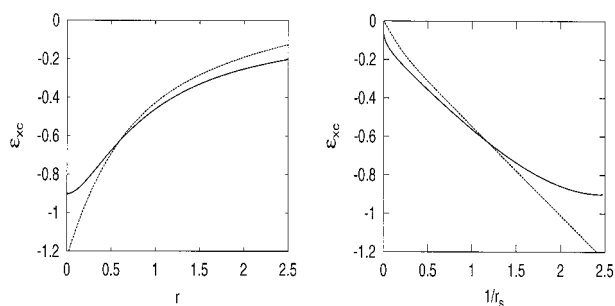


FIGURE 19. ε_{xc} for the He atom as given by the integral over the coupling constant and the exchange correlation hole from accurate data [60], full curves, and that used in one of the GGA approximations [165], dotted curves. Left, as a function of r , and, right, as a function of $1/r_s$ with $r_s = 3/(4\pi n)^{1/3}$, which would be a straight line for the uniform electron gas exchange-only approximation (a.u.).

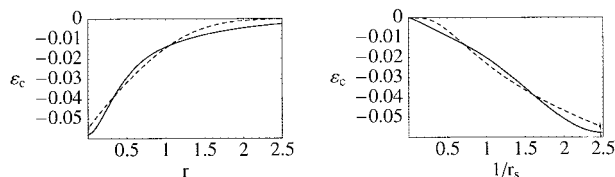


FIGURE 20. ε_c for the He atom as given by the integral over the coupling constant and the exchange correlation hole from accurate data [60], full curves, and that used in one of the GGA approximations [165], broken curves. Left, as a function of r , and, right, as a function of $1/r_s$ with $r_s = 3/(4\pi n)^{1/3}$.

It is interesting to note that, in the case of the He atom, the main difference of the GGA approximation considered for ε_{xc} comes from the exchange part and not for the correlation part (cf. Fig. 20).

It should be stressed, however, that this is not the unique way of seeing what ε_{xc} should be. A different way, not making use of the adiabatic connection, was proposed by Gritsenko et al. [166].* Figure 21 shows both curves. The abscissa has been chosen to be $1/r_s$, where r_s is a monotonous function of the radial distance, r , $r_s(r) = [3/(4\pi n(r))]^{1/3}$. In the X_α approximation ε_{xc} would be a line going through the origin with an adjustable slope. Note that both curves in Figure 21 come from accurate calculations [60], yielding the same, accurate E_c .

The source of this arbitrariness relies upon the attempt to fix a function, ε_{xc} , by knowing only a number, E_{xc} . Of course, one can add to the integrand any function that integrates to zero and obtain the same value for the integral.

Even when keeping to the adiabatic coupling via λ/r_{12} , one can use the exact formula [169]:

$$\begin{aligned} E_c[n] &= \int d\lambda \lambda^{-2} \sum_i [p_{ii}(\lambda) - p_{ii}(\lambda = 0)] \varepsilon_i \\ &= \int d^3 r n(r) \sum_i \int d\lambda \lambda^{-2} \\ &\quad \times [p_{ii}(\lambda) - p_{ii}(\lambda = 0)] \varepsilon_i |\varphi_i(r)|^2 / n(r) \quad (27) \end{aligned}$$

and identify $\varepsilon_c(r)$ with the sum in the last integral [ε_i are the KS eigenvalues, φ_i the KS orbitals, $p_{ii}(\lambda) = \int \varphi_i(r) \gamma(r, r'; \lambda) \varphi_i(r')$, and $\gamma(r, r'; \lambda)$ the first-order density matrix obtained at a given λ]. Weighting orbital quantities by $|\varphi_i(r)|^2$ may be “natural” but is

*See also Refs. [167, 168] for another interesting ways to define ε_{xc} .

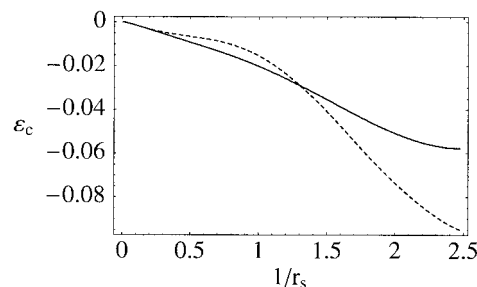


FIGURE 21. Adiabatic coupling (full curve) and formula of Gritsenko et al. (broken curve [166]) for ε_c as a function of $1/r_s$.

still arbitrary. We can thus think that we could construct ε_c by modeling $\int d\lambda \lambda^{-2} [p_{ii}(\lambda) - p_{ii}(\lambda = 0)]$. We show in Figure 22 $\int d^3 r n(r) \sum_i \int d\lambda \lambda^{-2} [p_{ii}(\lambda) - p_{ii}(\lambda = 0)] \varepsilon_i |\varphi_i(r)|^2 / n(r)$, together with the one obtained from the pair density, as a function of $1/r_s$. Although both yield by integration the same, correct correlation energy, their shape is totally different.

FUNCTIONAL FOR EXCHANGE AND CORRELATION, CORRELATION, OR A PART OF THEM?

It was often argued that the transferability works better when approximations are made for exchange

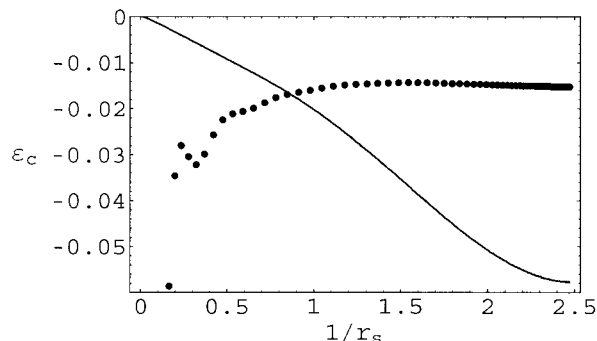


FIGURE 22. Accurate expression of functions that can be interpreted as ε_c for the He atom as a function of $1/r_s$. They were obtained using the adiabatic coupling λ/r_{12} , at constant density, using two different expressions of the correlation energy, one based upon the one-particle density matrix (points not connected), while the other was obtained using the two-particle density matrix (full curve) (a.u.). Although the calculations were performed with reasonably large Gaussian basis sets, their quality does not seem sufficient to describe well the behavior at small densities (small $1/r_s$).

and correlation together than when approximating just the correlation energy. This might be at first sight surprising, as correlation is just a significantly smaller quantity than exchange and correlation together. The arguments have different origins. Langreth and Perdew [170], for example, show that the leading long-range contribution that is specific for the uniform electron gas, and thus not transferable, cancels out when exchange and correlation are taken together. One also finds the argument based on the analysis of specific systems: that usual approximations for the correlation energy transfer just the dynamic correlation, while the static correlation is described by what should be the approximation of exchange only [171].

Especially the interest in properties determined by the asymptotic behavior of the potential brought back the interest to the so-called “exact” treatment of exchange, in the form of the optimized effective potential and its simplifications mentioned above.

A way to exploit the adiabatic connection formula is to write the integral over λ as $wP_2(r, r'; \lambda = 0) + (1 - w)P_2(r, r'; \lambda = 1)$, where w is an unknown weight [172]. The wave function at $\lambda = 0$ is determined in the KS process and considered known. Thus, $P_2(r, r'; \lambda = 0)$ is also known, containing just the parts appearing in the Coulomb and exchange energy expressions. $P_2(r, r'; \lambda = 1)$ is, of course, unknown. It is often argued that at strong interaction between electrons the effect of the external potential should be weaker and thus transferability from one system to the other should be better (see, e.g., [173, 174]). According to this philosophy, one should better make an approximation for $P_2(r, r'; \lambda = 1)$ than for $\int d\lambda P_2(r, r'; \lambda)$. One can thus think of a hybrid approach where

$$\begin{aligned} E_{xc}[n] &= \frac{1}{2} \int d^3r d^3r' \frac{1}{|r - r'|} \\ &\quad \times \int d\lambda [P_2(r, r'; \lambda) - n(r)n(r')] \\ &= w \frac{1}{2} \int d^3r d^3r' \frac{1}{|r - r'|} \\ &\quad \times [P_2(r, r'; \lambda = 0) - n(r)n(r')] \\ &\quad + (1 - w) \frac{1}{2} \int d^3r d^3r' \frac{1}{|r - r'|} \end{aligned}$$

$$\begin{aligned} &\times [P_2(r, r'; \lambda = 1) - n(r)n(r')] \\ &\approx w \frac{1}{2} \int d^3r d^3r' \frac{1}{|r - r'|} \\ &\quad \times [P_2(r, r'; \lambda = 0) - n(r)n(r')] \\ &\quad + (1 - w) \frac{1}{2} \int d^3r n(r) \varepsilon_{xc}(n(r), \dots). \end{aligned} \quad (28)$$

Note that the first integral on the right side is the exchange energy, justifying the name hybrid for this approach: Part of the exchange (w) is treated exactly (correlation equal to 0 at $\lambda = 0$), while for the other part exchange and correlation are treated together in an approximate way.* Of course, the weight w is system dependent (see, e.g., [166]). However, it turns out empirically that using w close to 1/4 gives good results in molecules when combined with simple functionals. (In the uniform electron gas it is closer to 1/3.) The success of a semiempirical functional, B3LYP [172, 175, 176], has highly contributed to an increasing popularity of hybrid functionals in molecular calculations.

For crystals, their application has been hampered by the missing of two-electron integrals in commonly used codes needed for computing $\int d^3r d^3r' (1/|r - r'|) [P_2(r, r'; \lambda = 0) - n(r)n(r')]^\dagger$.

The hybrid approach is not restricted to using the $\lambda = 0$ end-point. It can be used for other λ and, in fact, for other adiabatic connections, too.

It was argued before that it might be easier to transfer the short-range part of the electron-electron interaction energy and thus only a part of the (exchange-)correlation energy. To substantiate this point, we can consider what happens when μ in $\text{erf}(\mu r_{12})/r_{12}$ gets large. In that case, by using the Hellmann-Feynman formula and $\exp(-\mu^2 r_{12}^2) \rightarrow (\pi/\mu^2)^{3/2} \delta(r_1 - r_2)$, for $\mu \rightarrow \infty$, and δ being the 3-D Dirac delta function:

$$\begin{aligned} E_{xc, \mu \gg 0} - E_{xc, \mu \rightarrow \infty} \\ \approx \mu^{-2} \frac{\pi}{2} \int [P_2(r, r; \lambda) - n(r)n(r), \mu \rightarrow \infty] d^3r. \end{aligned}$$

A similar expression can be derived for the correlation-only part. Perdew and coworkers have

*As one uses approximations for ε_{xc} the KS orbitals will not be the exact ones and thus the exchange will not be exact either.

†An exception is the Crystal program [177].

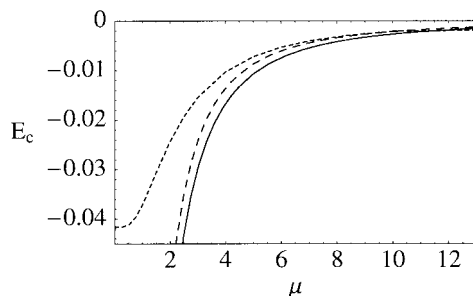


FIGURE 23. Correlation energy part not present in $e(\mu)$ as a function of μ in the adiabatic coupling $\text{erf}(\mu r_{12})/r_{12}$ (short-broken curve) from an accurate CI calculation. The exact asymptotic behavior, for large μ , to μ^{-2} , from an extremely accurate calculation (full curve) and its LDA approximation (long-broken curve) (a.u.).

shown in several studies (see, e.g., [178]) that the on-top pair density has good transferability from the uniform electron gas. We show in Figure 23 the evolution of the correlation energy, as a function of μ , for the He atom in the LDA approximation. On the same plot appears the asymptotic behavior obtained by using the formula above, using the data from an extremely accurate wave function [104] and that obtained by using the on-top pair density $P_2(r, r)$ of the uniform electron gas with density $n(r)$, as given by Yasuhara [179]. We see that the two last curves show a similar behavior. In fact, our configuration interaction (CI) calculation, which we qualify as “accurate” [60], yields a curve that is practically superimposed with that obtained by using the uniform electron gas information.*

In practice, we proceed in the opposite way, namely, advancing with accurate calculations toward larger μ . Thus, as we approach the curve of $E_{c,\mu \gg 0}$ we make increasingly smaller errors in transferring data from the uniform electron gas. Note, that, on one hand, the point where $E_{c,\mu \gg 0}$ starts giving negligible errors corresponds to small contributions coming from the uniform electron gas. On the other hand, we have to remember that this is not the only information we use. For example, when transferring data from the uniform electron gas the correlation energy correction term for He is finite, even at $\mu = 0$. Thus, the agreement between the exact and the LDA result becomes good even when an important part of the correlation energy is described by LDA (cf. Fig. 24).

*It is well known that obtaining an accurate on-top pair density is a much harder task than obtaining an accurate energy [180].

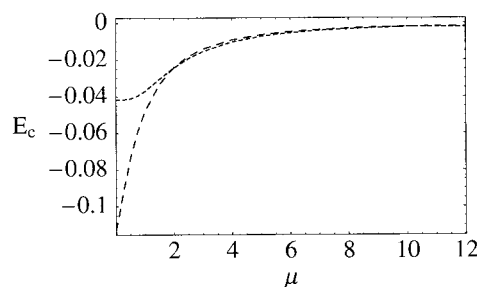


FIGURE 24. Correlation energy of the He atom, not present in $H(\mu)$ as a function of μ in the adiabatic coupling $\text{erf}(\mu r_{12})/r_{12}$ (short-broken curve) from an accurate CI calculation and in the LDA approximation (long-broken curve) (a.u.).

The next step is to ask whether one can use a small number of determinants when advancing to the value of μ that is large enough to make the LDA approximation work. We show in Figure 25 the evolution of the total energy of He, in the LDA approximation, as produced for different qualities of wave functions. (For other examples, see, e.g., [164].) Present experience shows that for $\mu \approx 1$ a good compromise can be reached.

Numerical calculations show that, as expected, the LDA works worse when near degeneracy is present. This is illustrated in Figure 26 for the hydrogen molecule, where the near-degeneracy effect increases with the interatomic separation. In such cases, the few determinants needed to describe the

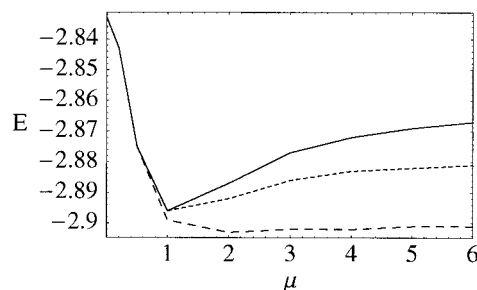


FIGURE 25. Energy within the LDA approximation for $E_{xc,\mu}[\eta]$ along the adiabatic connection using the coupling $\text{erf}(\mu r_{12})/r_{12}$ for the helium atom as a function of μ : calculated points connected by straight lines. The different curves correspond to an increasingly larger natural orbital space (the full lines connecting points obtained using just one Slater determinant, $1s^2$, the short-broken line correspond to the inclusion of the $2s^2$ determinant, while the long-broken line corresponds to a CI calculation within the space of the $1s^2, 2s^2, 3s^2, 2p^2, 3p^2, 3d^2$ [110] (a.u.).

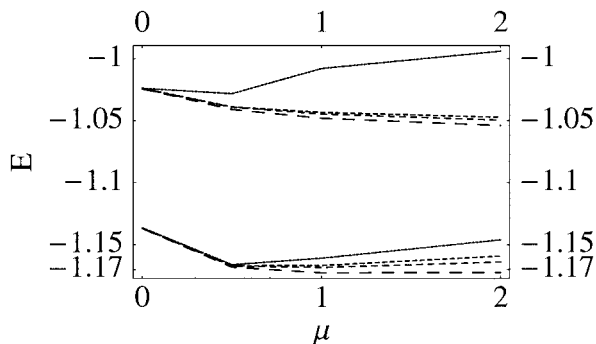


FIGURE 26. Energy within the LDA approximation for $E_{xc,\mu}[n]$ along the adiabatic connection using the coupling $\text{erf}(\mu r_{12})/r_{12}$ for the hydrogen molecule at equilibrium distance (lower group of curves) and at an interatomic distance of 3 bohr, as a function of μ : calculated points connected by straight lines. The different curves correspond to an increasingly larger orbital space (the full line connects points obtained using just the $1\sigma_g$ orbital and the broken line corresponds to the inclusion of the $1\sigma_u$ orbital, $2\sigma_g$, and the full CI calculation within our basis set [164] (dashing gets longer as the dimension of orbital space increases) (a.u.).

near-degeneracy effects should be included explicitly into the calculation of the $e(\mu)$.

Conclusion

The Hohenberg–Kohn theorem relies on the conjugate character of ground-state electron density $n(r)$ and external potential $v(r)$. This correspondence is rigorous but can also produce peculiar features, some of which were presented in this article. The KS method can be viewed as the calculation of a model system, to which a density functional $\bar{F}[n]$ is added, to enforce that the physical ground-state energy and density is produced when considering the model system. By modifying the model system, it is possible to switch continuously to the physical system by so-called “adiabatic connections.” In the KS system, the reference system is noninteracting and the corresponding wave function a single determinant. Modifying the Hamiltonian requires the inclusion of multideterminant wave function in the reference system. This seems to be important when near degeneracy is present. Further, this opens the way to a systematic improvement within DFT. However, there are many ways to exploit such a link, and little has been done along these lines.

There are many new exciting facets of DFT that were left out of this article. For example, more has to be said about the treatment of excited states and time-dependent DFT, the calculation of polarizabilities and hyperpolarizabilities, chemical shifts in nuclear magnetic resonance, core electron binding energies, etc. Powerful computational techniques were developed that allow a linear scaling with the size of a system.

The last decade has shown the uprise of many approximate density functionals, and the criteria for choosing one of the functionals is a matter of great importance for anyone applying them. No criteria were given for choosing the “best” functional. A reason for it is that, in the authors’ opinion, despite easy-to-use, highly efficient electronic structure codes, choosing the best calculation is still an art, and while statistics give a hint they cannot guarantee the quality of the result. There are several extensions of the KS method that were not treated in this article. In solid-state physics the method known as LDA+U has gained much importance for describing systems that are beyond the reach of the “classic” approximations of DFT. Another extension is designed for the treatment of van der Waals interactions. Methods simpler than KS also exist, and recent development for approximations of the kinetic energy raises hope for rapid calculations on huge systems. Last, but not least, DFT has permitted the development of important tools for chemistry, such as hardness or softness.

ACKNOWLEDGMENTS

The authors thank Prof. W. Kohn (University of California at Santa Barbara) for enlightening discussions, C. Gutle (Université Paris VI, France), and C. Umrigar (Cornell University) for helping them to produce some of the data shown in this article and Mark Casida for carefully reading and commenting on the article.

Appendix: Motivations for Using Ensembles

Besides being a physical manifestation, ensembles appear also in different contexts, which makes their inclusion important in DFT. Let us first consider the example of the dissociation or formation of molecules [97]. It shows that a change of the potential around the center X by another one, on

center Y, that is a large distance from that on X can significantly affect the ground-state density on X by charge transfer. The simplest relevant example is that of the A_2^+ molecule separating into A and A^+ . Symmetry dictates that the charge is evenly distributed between the two fragments. The density thus obtained on each of the centers is the average of those obtained in calculating the fragments A and A^+ isolated. Of course, the number of electrons on each site is also the average between that in A, N_A , and that in A^+ , $N_A - 1$, namely, $N_A - 1/2$. The average electron number per site is thus noninteger. As the fragments are separated by an infinite distance, we know that the energy of the composite system is equal to the sum of the energies of A and A^+ , ($E[N_A, \nu_A] + E[N_A - 1, \nu_A]$). Quantum mechanics ensures that the energy of this system, having a noninteger electron number on each of the sites, $2E[N_A - 1/2, \nu]$, is close to $E[N_A, \nu_A] + E[N_A - 1, \nu_A]$. Due to the separation of the fragments, we would like to be able to obtain the same result when considering the densities on each of the fragments. For doing it, we should be able to compute $E[N_A - 1/2, \nu]$. By considering the charged cluster A_m^{q+} the previous reasoning is easily extended to having an arbitrary fractional electron number $N_A - q/m$ on each site. The density on each of the site is thus given as an ensemble density:

$$n_A = \sum_i w_i n_{A,i}$$

each of the densities $n_{A,i}$ yielding an integer number, $N_{A,i}$ while the number of electrons in the ensemble is not necessarily integer:

$$N_A = \sum_i w_i N_{A,i}$$

Further,

$$E[N_A, \nu] = \sum_i w_i E[N_{A,i}, \nu_A]$$

In the approach above it was supposed that the functional is defined for $n + \delta n$. As long as the number of particles is kept fixed to an integer number N , there is no conceptual problem with this. One can imagine procedures where the search for the minimum is done by keeping N fixed. However, by introducing the Lagrange multipliers to keep N fixed, which is the common way of proceeding, the

search process is done for functionals of a density integrating to any number of electrons. One can think in terms of ensembles to have functionals defined for a noninteger number of electrons.

Ensembles also appear in density functional calculations using fictitious Hamiltonians, to be discussed in more detail below. Degeneracies show up that are not present in the physical system. Thus, for the correct KS treatment one has to proceed carefully treating degeneracies.

Although ensembles were slow to enter classic quantum chemistry codes, they were used for many years in X_α calculations (see, e.g. [87]), and many calculations, e.g., for metallic clusters, would not be possible without them. Working with ensembles allows production of good algorithms to ensure convergence in the solution of the KS equations [181].

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