A simple, clear and pedagogical way of introducing Density Functional Theory[†]

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Abstract

Density functional theory (DFT) plays a crucial role in computational chemistry, but its introduction in the chemistry curricula poses a challenge to lecturers when it comes to laying down its foundation without using a complex mathematical formalism and to establishing its scope and limitations. This article aims at presenting a simple and clear derivation of the theory that shows up its very general character. It is based on the constrained-search approach, that bears a close parallelism with the wave-function variational theorem, a familiar tool in

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any quantum chemistry introduction. Notwithstanding its simplicity, this approach shows appealing features, such as providing an explicit connection of the ground-state density with the electronic hamiltonian and an expression for the universal functional appearing in the definition of the energy functional. These lead to a more tangible insight into the theory than the original derivation by Hohenberg and Kohn, which only guarantees the existence of that connection and this functional. On the other hand, the approach highlights that the theory may, in principle, treat open and closed shell ground states on an equal footing, without the need to impose any restriction about the state spin. An interesting result is recalled that guarantees that a Kohn-Sham scheme may always be set up, no matter the open or closed shell character of the ground state nor its degree of electron correlation.

Introduction

During the last decades *Density Functional Theory* (DFT) has become an essential tool for molecular and material modeling.[1] It has allowed a great leap towards the popularization of computational tools even among non-quantum chemists that were once foreign to quantum methodology. Two main factors have contributed to this change: the simplicity of DFT calculations as compared with rigorous wave function-based methods, and their excellent cost-to-performance ratio, that makes it possible to study fairly complicated systems with very affordable hardware.

DFT tackles the problem of calculating electronic energies and other properties of many-electron systems with a different strategy than that of the wave function-based methods. These are normally introduced in quantum chemistry programs by first describing the Hartree-Fock method as the simplest approach for obtaining approximate electronic wave functions. These are Slater determinants that admit a straightforward interpretation in terms of orbitals that can be occupied by one or two electrons. Then post-Hartree-Fock methods are introduced to obtain more accurate wave functions in order to correct the flaws of the orbital approximation. DFT does not fit into this scheme, since it aims at obtaining the ground-level electron density and energy of a many-electron system without actually calculating its wave function. A major advantage here is that the density

is a function of only three variables —the position coordinates x,y,z— regardless of the number of electrons, while the wave function depends on four coordinates —three spatial and one of spin— for each electron.

The usual way of introducing DFT follows an historical perspective: from the precedents of Thomas[2] and Fermi[3] in 1927 to the statement of the two foundational theorems by Hohenberg and Kohn (HK) in their 1964 seminal article.[4] In 1979 the constrained-search (CS) approach was put forward by Levy[5] and Lieb[6] following an earlier proposal by Percus.[7] This approach is conceptually clear and elegant, and bears a close parallelism with the wave-function variational theorem, which is deeply rooted in quantum chemistry. Most importantly, it is more general and rigorous that the original HK formulation, which was restricted to non-degenerate ground states and relied on the assumption that the trial densities appearing in their variational theorem correspond to ground state wave functions of many-electron systems (pure-state v-representability), which is not generally true.[6] Both limitations are superseded in the constrained-search (CS) approach. Moreover, this provides an algorithm connecting the density with the hamiltonian and an explicit expression for the universal term of the energy functional, while the HK derivation only guarantees the existence of that connection and this functional.

In this article the CS approach will be presented following a simple, lesser-known derivation published by Levy in 2001,[8] which uses only basic mathematical tools available in any introductory quantum chemistry text book. Some criticism about a pretended need to impose spin or symmetry restrictions on the density for open shell systems[9] will be shown to be unfounded. The most widespread practical implementation of the theory –the Khon-Sham (KS) method[10]– will also be briefly discussed. This relies on an assumption made by KS that has been the subject of intense debate: the existence of a non-interacting many-electron system with the same ground-level density as the real interacting one; that is, the non-interacting v-representability of the density. Work by Chayes *et al.* in 1985[11] and specially by van Leeuwen in 2003[12] clarifies this point and guarantees that a conveniently generalized KS scheme may always be applied.

We hope to contribute to encourage lecturers to use the present approach for introducing DFT

into their quantum chemistry curricula.

One-electron density

Although the formalism is more general, we will refer to an n-electron system under the attraction of one or more nuclei, typically an atom, a molecule or a solid. Its non-relativistic electronic hamiltonian is:

$$\widehat{H} = \widehat{T_{el}} + \widehat{V_{el}} + \widehat{V_{nuc-el}} \tag{1}$$

where $\widehat{T_{el}}$, $\widehat{V_{el}}$ and $\widehat{V_{nuc-el}}$ are the operators corresponding to the n-electron kinetic, repulsion and nuclear attraction energies:[13]

$$\widehat{T_{el}} = \sum_{i=1}^{n} -\frac{\nabla_i}{2} \qquad \widehat{V_{el}} = \sum_{i=1}^{n-1} \sum_{j>i}^{n} \frac{1}{r_{ij}} \qquad \widehat{V_{nuc-el}} = \sum_{i=1}^{n} v_{ne}(\vec{r}_i) \tag{2}$$

The one-electron term

$$v_{ne}(\vec{r}_i) = \sum_{A=1}^{N} -\frac{Z_A}{r_{iA}} \tag{3}$$

is referred to as the *external potential*, meaning that it represents the interaction of an electron (i) with something external to the n-electron system: the nuclei (A). This is a multiplicative, spin-independent operator and, in fact, all the discussion below is valid for any external potential of that kind.

The *one-electron density* (for short, "the density") corresponding to any normalized n-electron wave function Ψ can be obtained by integrating it with respect of all the space and spin coordinates ($\vec{r}_i$ and ω_i) except the position coordinates of one of the electrons:[14]

$$\rho(\vec{r}) = n \int_{\omega_1} \int_{\vec{r}_2} \int_{\omega_2} \ldots \int_{\vec{r}_n} \int_{\omega_n} |\Psi(\vec{r}, \omega_1, \vec{r}_2, \omega_2, \ldots \vec{r}_n, \omega_n)|^2 \, d\omega_1 d\vec{r}_2 d\omega_2 \ldots d\vec{r}_n d\omega_n \tag{4}$$

The definite integrals in this equation highlight that there is an infinity of wave functions leading to

a given density. Since Ψ is normalized to 1, the density is normalized to the number of electrons:

$$
\begin{aligned}
\int_{\vec{r}} \rho(\vec{r}) d\vec{r} &= n \int_{\vec{r}} \int_{\omega_1} \int_{\vec{r}_2} \int_{\omega_2} \cdots \int_{\vec{r}_n} \int_{\omega_n} |\Psi(\vec{r}, \omega_1, \vec{r}_2, \omega_2, \ldots \vec{r}_n, \omega_n)|^2 \, d\vec{r} d\omega_1 d\vec{r}_2 d\omega_2 \ldots d\vec{r}_n d\omega_n \\
&= n \langle \Psi | \Psi \rangle = n
\end{aligned}
\tag{5}
$$

According to the time-independent Schrödinger equation the energies of the stationary states of the electron system are the eigenvalues E_j of the hamiltonian:

$$
\widehat{H} \Psi_{jk} = E_j \Psi_{jk} \qquad k = 1, \ldots d_j
$$

where d_j is the degeneracy of eigenvalue E_j and $\{\Psi_{j1}, \cdots \Psi_{jd_j}\}$ are d_j linearly independent eigenfunctions with that eigenvalue. If Ψ is not an eigenfunction of the hamiltonian the corresponding state has not a well-defined energy, but we can calculate an energy expectation value by solving the integral:

$$
\left\langle \Psi \left| \widehat{H} \Psi \right. \right\rangle = \int_{\vec{r}_1} \int_{\omega_1} \cdots \int_{\vec{r}_n} \int_{\omega_n} \Psi^* \widehat{H} \Psi \, d\vec{r}_1 d\omega_1 \cdots d\vec{r}_n d\omega_n
$$

This can be broken down into two terms by introducing eq. (1):

$$
\left\langle \Psi \left| \widehat{H} \, \Psi \right. \right\rangle = \left\langle \Psi \left| \left(\widehat{T_{el}} + \widehat{V_{el}} \right) \Psi \right. \right\rangle + \left\langle \Psi \left| \widehat{V_{nuc-el}} \, \Psi \right. \right\rangle
$$

Let us show that the last term, namely, the nuclei-electron attraction energy, is determined by the electron density:

$$
\begin{aligned}
\left\langle \Psi \left| \widehat{V_{nuc-el}} \Psi \right. \right\rangle &= \int \Psi^* \left(\sum_{i=1}^{n} v_{ne}(\vec{r}_i) \right) \Psi \, d\vec{r}_1 d\omega_1 \ldots d\vec{r}_n d\omega_n \\
&= \sum_{i=1}^{n} \int_{\vec{r}_1} \int_{\omega_1} \cdots \int_{\vec{r}_n} \int_{\omega_n} v_{ne}(\vec{r}_i) |\Psi|^2 \, d\vec{r}_1 d\omega_1 \ldots d\vec{r}_n d\omega_n
\end{aligned}
$$

Since $|\Psi|^2$ is symmetric with respect to exchanges of electron coordinates and v_{ne} has the same mathematical expression for every electron, all the terms in the sum are equal, and we can write it

as n times the first term:

$$\left\langle \Psi \left| \widehat{V_{nuc-el}} \Psi \right. \right\rangle \;=\; n \int_{\vec{r}_1} v_{ne}(\vec{r}_1) \left(\int_{\omega_1} \cdots \int_{\vec{r}_n} \int_{\omega_n} |\Psi(\vec{r}_1, \omega_1, \ldots \vec{r}_n, \omega_n)|^2 \, d\omega_1 \ldots d\vec{r}_n d\omega_n \right) d\vec{r}_1$$

We can now introduce eq. (4) to obtain:

$$\left\langle \Psi \left| \widehat{V_{nuc-el}} \Psi \right. \right\rangle = \int_{\vec{r}_1} v_{ne}(\vec{r}_1) \rho(\vec{r}_1) d\vec{r}_1 \tag{6}$$

Of course, the same applies to any other property whose operator is a sum of multiplicative, spin-independent, one-electron operators, such as the components of the electric dipole moment ($d_x \equiv \sum_{i=1}^{n} q_i x_i, \cdots$), those of the electric quadrupole moment ($Q_{xx} \equiv \sum_{i=1}^{n} q_i x_i^2, \cdots$), etc. For short, we will refer to such properties as "one-electron multiplicative properties". All of these are, therefore, "functionals" of the density ρ; that is, (real) functions that depend on the variable ρ. This type of dependency is usually represented with brackets: $V_{nuc-el}[\rho]$, $d_x[\rho]$, $Q_{xx}[\rho]$, etc.

The variational HK theorem

The variational HK theorem states that the ground-level energy E_0 of an n-electron system is the minimum of a functional of the electron density $E[\rho]$ with respect to densities corresponding to whatever n-electron states:

$$\boxed{E_0 = \min_{\rho} E[\rho]} \tag{7}$$

where

$$E[\rho] = F[\rho] + \int_{\vec{r}} v_{ne}(\vec{r}) \rho(\vec{r}) d\vec{r} \tag{8}$$

and $F[\rho]$ is a universal functional; namely, it is independent of the particular n-electron system being considered.

To prove it let us recall the standard wave-function variational theorem, which states that any wave function Ψ of the n-electron (antisymmetric) Hilbert space $\mathscr{H}$ leads to an energy expectation

6

value –the variational integral– not lower than the ground-level energy:

$$\left\langle \Psi \left| \hat{H} \, \Psi \right. \right\rangle \geq E_0$$

so that E_0 can be obtained by minimizing the variational integral over the whole antisymmetric wave-function space $\mathcal{H}$:

$$E_0 = \min_{\Psi \in \mathcal{H}} \left\langle \Psi \left| \hat{H}\Psi \right. \right\rangle \tag{9}$$

This minimization can be performed in two steps:

1. For any given density ρ we minimize $\left\langle \Psi_\rho \left| \hat{H}\Psi_\rho \right. \right\rangle$ with respect to all the wave functions Ψ_ρ leading to that density. This gives a real number that depends on ρ —that is, a functional of the density ρ— that will be referred to as the *energy functional*:

$$E[\rho] \equiv \min_{\Psi_\rho} \left\langle \Psi_\rho \left| \hat{H}\Psi_\rho \right. \right\rangle = \left\langle \Psi_\rho^{min} \left| \hat{H}\Psi_\rho^{min} \right. \right\rangle \tag{10}$$

where Ψ_ρ^{min} is the minimizing Ψ_ρ.

2. Then $E[\rho]$ is minimized with respect to the densities of all the n-electron states (eq. 7).

Let us introduce eq. (1) in (10):

$$E[\rho] = \min_{\Psi_\rho} \left(\left\langle \Psi_\rho \left| \left(\widehat{T_{el}} + \widehat{V_{el}} \right) \Psi_\rho \right. \right\rangle + \left\langle \Psi_\rho \left| \widehat{V_{nuc-el}}\Psi_\rho \right. \right\rangle \right) \tag{11}$$

The last integral is the same for all Ψ_ρ with the same density ρ (eq. 6), so Ψ_ρ^{min} also minimizes the first term, and we can define a new functional $F[\rho]$ as:

$$\boxed{F[\rho] \equiv \min_{\Psi_\rho} \left\langle \Psi_\rho \left| \left(\widehat{T_{el}} + \widehat{V_{el}} \right) \Psi_\rho \right. \right\rangle = \left\langle \Psi_\rho^{min} \left| \left(\widehat{T_{el}} + \widehat{V_{el}} \right) \Psi_\rho^{min} \right. \right\rangle} \tag{12}$$

Introducing eqs. (12) and (6) in (11) one obtains eq. (8).

The operators $\widehat{T_{el}}$ and $\widehat{V_{el}}$ are completely determined by the number of electrons (eq. 2), which

is readily obtained by integrating ρ (eq. 5); therefore, $F[\rho]$ is independent of the particular n-electron system being considered; namely, it is a *universal* functional. If we had an accurate enough expression of $F[\rho]$ for some n then, by adding the nuclei-electron attraction energy term of whatever n-electron system (eq. 6) and minimizing the resulting $E[\rho]$ we would obtain its ground-level energy and density. Obtaining $F[\rho]$ is the sticking point in DFT, and several strategies have been devised to this end, including the Kohn-Sham method, to be briefly discussed later.

Some points should be made:

1. The minimization of $E[\rho]$ should be restricted to trial densities coming from (antisymmetric) wave functions of the n-electron Hilbert space (n-representable densities), since eq. (12) only defines $F[\rho]$ for such densities. This requirement is weaker than the v-representability needed for the HK deduction –that is, the necessity of coming from a ground state of some n-electron hamiltonian– and, according to theorems 1.1 and 1.2 of ref. 6, it is fulfilled by the necessary and sufficient conditions:

$$\rho(\vec{r}) \geq 0 \qquad \int_{\vec{r}} \rho(\vec{r}) d\vec{r} = n \qquad \int_{\vec{r}} \left| \vec{\nabla} \sqrt{\rho(\vec{r})} \right|^2 d\vec{r} < \infty$$

The first two are immediate consequences of the definition of ρ (see eqs. (4) and (5)), and the third is fulfilled for any system with finite kinetic energy, since it can be shown that $\int_{\vec{r}} \left| \vec{\nabla} \sqrt{\rho(\vec{r})} \right|^2 d\vec{r} \leqslant 2 \left\langle \Psi \left| \widehat{T} \Psi \right. \right\rangle$ (see the appendix).

2. The existence of a minimizing wave function Ψ_ρ^{min} in (eq. 12) is guaranteed by theorem 3.3 of ref. 6.

3. The functional $F[\rho]$ is universal in the sense that it is independent of the particular form of the external potential $v_{ne}(\vec{r}_i)$, but it depends on the number of electrons n.

4. The above demonstration applies no matter the degeneracy of the ground level, unlike the original HK one. If the ground level is degenerate the minimizations in (10) or (12) and (7) would lead to the density of one of the degenerate ground states.

5. It has been claimed that spin and space symmetry restrictions must be imposed to the trial densities when minimizing $E[\rho]$ for an open shell ground level[15]. The present approach makes clear that such restrictions are unnecessary, as they also are for the trial wavefunctions in the standard variational method. If such restrictions were necessary because some non-restricted antisymmetric wave functions existed with lower energy than the restricted minimum, we could expand that non-restricted function as a linear combination of restricted functions, and at least one of these should have a lower energy than the non-restricted one. This would mean that the minimization process has not explored the whole antisymmetric Hilbert space. The ground level of any quantum system is the lowest eigenvalue of its hamiltonian, which, in turn, is the lowest value of $\left\langle \Psi \middle| \widehat{H} \Psi \right\rangle$ for Ψ's in the antisymmetric Hilbert space –that may include boundary conditions implied by the physical problem– and, according to quantum principles, no additional restrictions need to be imposed for obtaining it.

6. Last, but not least, the present approach provides an expression for the functional $F[\rho]$ (eq. 12), while the original HK demonstration only guarantees its existence. Equation (12) has been recently used to obtain $F[\rho]$ for a unidimensional 2-electron system with a softened Coulomb interaction.[16]

7. Lieb[6] introduced an alternative universal functional in which the expectation value of $\widehat{T_{el}} + \widehat{V_{el}}$ is calculated and minimized in terms of density operators instead of wave functions (eq. 12). Although it has some mathematical benefits compared to the functional (12) we will not discuss it here because it exceeds the level of basic quantum chemistry curricula.

The ground-level density determines the external potential

Hohenberg and Khon also demonstrated that the ground-state density $\rho_0(\vec{r})$ of an n-electron system determines the external potential except for an irrelevant additive constant.

Let us assume that the ground-level E_0 has degeneracy d_0. We will use Ψ_0 to refer to one of

the corresponding wave functions and ρ_0 for its electron density. According to the wave-function variational theorem (eq. 9) Ψ_0 minimizes $\left\langle \Psi \middle| \widehat{H}\,\Psi \right\rangle$ with respect to any wave function of the Hilbert space and, in particular, with respect to all of the wave-functions Ψ_{ρ_0} with density ρ_0: $\Psi_0 = \Psi_{\rho_0}^{min}$. We have already seen that $\Psi_{\rho_0}^{min}$ also minimizes $\left\langle \Psi_{\rho_0} \middle| \left(\widehat{T_{el}} + \widehat{V_{el}}\right) \Psi_{\rho_0} \right\rangle$ (see eq. (12) and the discussion that precedes it):

$$\Psi_0 = \Psi_{\rho_0}^{min} \qquad \text{where "min" refers to} \qquad \min_{\Psi_{\rho_0}} \left\langle \Psi_{\rho_0} \middle| \left(\widehat{T_{el}} + \widehat{V_{el}}\right) \Psi_{\rho_0} \right\rangle \qquad (13)$$

By performing this minimization one can thus obtain Ψ_0 from ρ_0, something that has been called into question in ref. 9. In case of degeneracy, any one of the ground-level wave functions could be obtained, depending on the evolution of the minimization process,

By introducing eqs. (1) and (2) into the Schrödinger equation:

$$\widehat{H}\Psi_0 = \widehat{T_{el}}\Psi_0 + \sum_{i=1}^{n-1}\sum_{j>i}^{n}\frac{1}{r_{ij}}\Psi_0 + \sum_{i=1}^{n} v_{ne}(\vec{r}_i)\Psi_0 = E_0\Psi_0$$

and dividing by Ψ_0 we obtain:

$$\sum_{i=1}^{n} v_{ne}(\vec{r}_i) = E_0 - \frac{\widehat{T_{el}}\Psi_0}{\Psi_0} - \sum_{i=1}^{n-1}\sum_{j>i}^{n}\frac{1}{r_{ij}}$$

If we don't know E_0, $\sum_{i=1}^{n} v_{ne}(\vec{r}_i)$ is determined except for an additive constant, that can be obtained by fixing the origin of the energy scale.

We have already seen that the first two terms $\widehat{T_{el}}$ and $\widehat{V_{el}}$ of the hamiltonian (1) are determined by n which, in turn, is determined by ρ_0 (eq. 5). So this density determines, in fact, the complete electronic hamiltonian:

$$\boxed{\rho_0 \longrightarrow \Psi_0 \longrightarrow v_{ne} \longrightarrow \widehat{H}}$$

Note that:

1. The degeneracy of E_0 is, again, irrelevant to the preceding derivation, while the original HK

demonstration required the ground state to be non-degenerate.

2. To obtain Ψ_0 from ρ_0 no information about the spin and/or space symmetry of the ground state, needs to be imposed (apart, of course, of the exchange antisymmetry inherent in the antisymmetric Hilbert subspace), which contradicts the statement in ref. 9: "one may incorrectly claim that ρ_0 does also determine the ground state wave function".

3. The present approach provides an explicit recipe for obtaining the external potential from ρ_0, while the original proof only assures that a dependency relationship exists.

4. Since the eigenfunctions of $\hat{H}$ determine all the properties of the corresponding electronic states, all of these –not only the ground state energy and one-electron multiplicative properties– are determined by ρ_0, albeit, in general, we do not know how to obtain them without calculating the corresponding wave-functions or, at least, their 2-particle density matrices (see ref.[17] for work along this line).

5. For a degenerate ground level it can be shown[12] that, not only the densities ρ_{0k} corresponding to individual eigenfunctions Ψ_{0k}, with $k = 1, \cdots d_0$, determine $\hat{H}$, but also any "ensemble" density of the form $\rho_0 = \sum_{k=1}^{d_0} \lambda_k \rho_{0k}$ with $\sum_{k=1}^{d_0} \lambda_k = 1$ does.

6. The fact that v_{ne} is determined by ρ_0 admits a simple physical interpretation: ρ_0 has peaks on the nuclei with a slope related to the nuclear charge, so that it is reasonable that the position and charge of the nuclei and, therefore, v_{ne} (see eq. 3) can be obtained from ρ_0.

The Khon-Sham implementation

One year after the publication of the HK theorems, Khon-Sham (KS) published a method for putting those ideas into practice. This consists in looking for a fictitious system of n electrons that move independently under an external potential $v_{KS}(\vec{r})$ such that its ground-state density is equal to that of the real system. Then an approximate universal functional is used to obtain the

energy of this system. Since the electrons of the fictitious system do not interact with each other, its hamiltonian eigenfunctions can be taken as Slater determinants, and an algorithm similar to the Hartree-Fock method can be settled to obtain them. Moreover, although the ground state of this non-interacting system bears no direct relationship to that of the real system, the interpretation of their obtitals in a way similar to that of the Hartree-Fock orbitals has proven to be fruitful.

We will not go into the details of the KS method, but we want to clarify some points about the conjecture made by Khon and Sham about the existence of a proper non-interacting system for every real system. If such a system exists with a ground state Slater determinant (or a linear combination of degenerate Slater determinants) with density equal to that of the real system we say that this density is *non-interacting pure-state v*-representable. In the degenerate case it could happen that no density ρ_{0k} corresponding to an individual non-interacting wave function coincides with that of the real system, but a linear combination of the form $\rho_0 = \sum_{k=1}^{d_0} \lambda_k \rho_{0k}$ does, in which case we say that this is *non-interacting ensemble v*-representable (NI-E-R). This is in fact the case for some strongly correlated systems and for near-degeneracy situations such as in avoided crossings, among others. Although we currently don't known if the sets of interacting ensemble *v*-representable (I-E-R) and NI-E-R densities are equal, it has been proven[12] that for every I-E-R density –as is any ground level density of any real system– one can find a NI-E-R density arbitrarily close. Therefore, a KS scheme can always be set up provided that it allows for ensemble densities.[12,18]

Note that we have not mentioned unrestricted Slater determinants, so that no splitting of the density in alpha and beta components should, in principle, be necessary to reproduce the density of real open shell systems.

Conclusions

The constrained-search approach to density functional theory is presented in a simple way particularly suitable for quantum chemistry curricula. The derivation of the Hohenberg-Kohn variational

theorem highlights its close parallelism with the wave-function variational method, that plays a central role in other computational chemistry methods. Contrary to the original formulation by Hohenberg and Kohn, the present approach is not restricted to non-degenerate ground states, so it applies to closed and open shell systems indistinctly without the need to impose any restriction beyond the antisymmetry of the wave functions. Moreover, the former is affected by the unsolved problem of the v-representability requirement for trial densities, while the constrained-search derivation only necessitates the weaker n-representability, for which explicit necessary and sufficient conditions are known. On the other hand, it provides an expression for the universal functional $F[\rho]$ appearing in the definition of the energy functional and an algorithm to derive the electronic hamiltonian from the ground-state electron density, while the original formulation only guarantees the existence of that functional and of a dependency relationship of the hamiltonian with respect to the density. Besides their potential interest for the development of computational strategies, those two points make the constrained-search approach more tangible and appealing from the pedagogical point of view. For all this we consider it the most convenient way of introducing density functional theory in basic quantum chemistry courses. The Khon-Sham scheme is also briefly discussed and an interesting result by van Leeuwen is recalled that guarantees that a Kohn–Sham scheme can always be set up provided that it allows for ensemble densities, not even being necessary to split de density in alpha and beta contributions for open shell systems.

Appendix

Differentiation of eq. (4) and use of the Cauchy–Schwarz inequality leads to

$$
\begin{aligned}
\left|\vec{\nabla}_1\rho(\vec{r}_1)\right|^2 &= \left(\frac{\partial\rho(\vec{r}_1)}{\partial x_1}\right)^2 + (x_1 \to y_1) + (x_1 \to z_1) \\
&= n^2 \left[\left(\frac{\partial \int |\Psi|^2 d\omega_1 d\vec{r}_2\cdots d\omega_n}{\partial x_1}\right)^2 + (x_1 \to y_1) + (x_1 \to z_1)\right] \\
&= n^2 \left[\left(\int \frac{\partial |\Psi|^2}{\partial x_1} d\omega_1 d\vec{r}_2\cdots d\omega_n\right)^2 + (x_1 \to y_1) + (x_1 \to z_1)\right] \\
&= n^2 \left[\left(\int 2|\Psi|\frac{\partial |\Psi|}{\partial x_1} d\omega_1 d\vec{r}_2\cdots d\omega_n\right)^2 + (x_1 \to y_1) + (x_1 \to z_1)\right] \\
&\leq n^2 4 \int |\Psi|^2 d\omega_1 d\vec{r}_2\cdots d\omega_n \left[\int \left(\frac{\partial |\Psi|}{\partial x_1}\right)^2 d\omega_1 d\vec{r}_2\cdots d\omega_n + (x_1 \to y_1) + (x_1 \to z_1)\right] \\
&= 4n\rho(\vec{r}_1) \int \left|\vec{\nabla}_1\Psi\right|^2 d\omega_1 d\vec{r}_2\cdots d\omega_n
\end{aligned}
$$

so that

$$
\begin{aligned}
\int \left|\vec{\nabla}_1\sqrt{\rho(\vec{r}_1)}\right|^2 d\vec{r}_1 &= \int \left[\left(\frac{\partial\sqrt{\rho(\vec{r}_1)}}{\partial x_1}\right)^2 + (x_1 \to y_1) + (x_1 \to z_1)\right] d\vec{r}_1 \\
&= \int \left[\left(\frac{1}{2\sqrt{\rho(\vec{r}_1)}}\frac{\partial\rho(\vec{r}_1)}{\partial x_1}\right)^2 + (x_1 \to y_1) + (x_1 \to z_1)\right] d\vec{r}_1 \\
&= \int \left[\frac{1}{4\rho(\vec{r}_1)}\left|\vec{\nabla}\rho(\vec{r}_1)\right|^2\right] d\vec{r}_1 \\
&\leq n \int \left|\vec{\nabla}_1\Psi\right|^2 d\vec{r}_1 d\omega_1 d\vec{r}_2\cdots d\omega_n \\
&= n \int \left[\frac{\partial\Psi^*}{\partial x_1}\frac{\partial\Psi}{\partial x_1} + (x_1 \to y_1) + (x_1 \to z_1)\right] d\vec{r}_1 d\omega_1 d\vec{r}_2\cdots d\omega_n \\
&= n \left[\langle\widehat{p_{x_1}}\Psi|\widehat{p_{x_1}}\Psi\rangle + (x_1 \to y_1) + (x_1 \to z_1)\right] \\
&= n \left[\left\langle\Psi\left|\widehat{p_{x_1}}^2\Psi\right.\right\rangle + (x_1 \to y_1) + (x_1 \to z_1)\right] \\
&= 2\left\langle\Psi\left|\widehat{T}\Psi\right.\right\rangle
\end{aligned}
$$

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(13) Atomic units will be used thorough this paper: $m_e = 1$, $e = 1$, $\hbar = 1$, $4\pi\varepsilon_0 = 1$.

(14) All wave functions will be assumed antisymmetric with respect to exchange of the coordinates of any pair of electrons, as required by the Pauli principle.

(15) In ref. 9 it is stated that "anti-symmetry and spin restrictions are imposed on the wave function to satisfy the Pauli principle and spin symmetry requirements",… "spin symmetry restrictions need to be imposed even on the Full Configuration Interaction wave function … Neglecting this constraint would result in broken symmetry solutions where the total spin is no longer defined",… "It is customary to expand Ψ in a known basis set and to find the expansion coefficients using the variational method and with all necessary and sufficient constraints (spin and space symmetries) to prevent the variational collapse",

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