Density functional theory versus
the Hartree Fock method: comparative assessment

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Abstract

We compare two different approaches to investigations of many-electron systems. The first is the Hartree-Fock (HF) method and the second is the Density Functional Theory (DFT). Overview of the main features and peculiar properties of the HF method are presented. A way to realize the HF method within the Kohn-Sham (KS) approach of the DFT is discussed. We show that this is impossible without including a specific correlation energy, which is defined by the difference between the sum of the kinetic and exchange energies of a system considered within KS and HF, respectively. It is the nonlocal exchange potential entering the HF equations that generates this correlation energy. We show that the total correlation energy of a finite electron system, which has to include this correlation energy, cannot be obtained from considerations of uniform electron systems. The single-particle excitation spectrum of many-electron systems is related to the eigenvalues of the corresponding KS equations. We demonstrate that this spectrum does not coincide in general with the eigenvalues of KS or HF equations.

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I. INTRODUCTION

The Hartree-Fock method (HF) originate from the pioneer works of Hartree [1] and Fock [2]. Since then an impressive progress has been achieved by using HF as a basis when calculating the ground state energy and constructing the Random Phase Approximation (RPA) and the Random Phase Approximation with Exchange (RPAE) to investigate the dynamic properties of multi-electron objects, such as atoms [3], molecules, clusters and fullerenes. Unfortunately, HF method has a number of difficulties in its application. For instance, one needs a whole set of single-particle wave functions to calculate the single-electron nonlocal potential. It is also necessary to follow a rather intricate procedure to include the correlation corrections that are beyond the HF framework. As a result, in the case of complex many-electron systems, starting with molecules, that include at least several atoms, the calculations become too complicated.

The Density Functional Theory (DFT) that was invented in the early 1960s has, generally speaking, overcome these difficulties. DFT has reduced the problem of calculating the ground state characteristics of a many-electron system in a local external field to the solution of the Hartree-like one-electron equations [4–6]. At first DFT was limited to consideration of only the ground states of many-electron systems, leaving aside their dynamic properties, which are closely related to the systems behavior in the time-dependent external fields. This limitation of DFT was surmounted by Runge and Gross [7] by transforming DFT into the so-called Time-Dependent Density Functional Theory (TDDFT), which in fact is a quite natural generalization of DFT.

Both DFT and TDDFT are based on the one-to-one correspondence between the particle densities of the considered systems and external potentials acting upon these particles. For definiteness, we assume that the time dependent part of the considered electronic system’s density \( \rho(\mathbf{r}, t) \), which is created under the action of an external time-dependent field \( \lambda v_{\text{ext}}(\mathbf{r}, t) \), is developing from the system’s ground state. Consequently, one can conclude that the wave function and each observable, describing the system, can be presented as a functional of the density. Examples are the functionals of the ground state energy \( E[\rho] \) and of the action \( A[\rho] \) [5–7].

DFT and TDDFT establish an exact correspondence between a system of many interacting particles and a fictitious non-interacting Kohn-Sham (KS) system [5–8]. The main advantage of this “mapping” is that KS system is described by a set of Hartree-type single particle equations, which is not too difficult to solve. As a result, after solving these equations in the case of an external time-independent potential, one can obtain and predict, at least in principle, the atomic, molecular, cluster and solid bodies binding energies, phonon spectra, activation barriers etc. (see e.g. [6,8]). The same is true in the case of a time-dependent potential when the solution yields the single-particle and collective excitation spectra (see e.g. [8–11]).

Unfortunately, the one-to-one correspondence proved in [4,7] establishes the existence of the functionals only in principle, leaving aside a very important question on how one can construct them in reality. This is why the success of DFT and TDDFT strongly depends upon the availability of good approximations for the functionals. A systematic way to construct the required functionals and the corresponding response functions and effective interaction was suggested in a number of papers [9–11].

Since the HF and the Kohn-Sham theory play an important role in the many-body physics, it deserves comprehensive examinations in order to reveal their shortcomings and advantages as compared to one another when applied to studies of the many-electron systems. Recently, a key
element of DFT, the action functional $A[\rho]$, was suspected to be ill-defined because of a number of contradictions in it. It appeared that the contradiction, which came from the analysis of the causality and symmetry properties of the linear response functions in TDDFT, plays the central role in creating other contradictions [8,12,13]. Fortunately, these contradictions were successfully resolved recently [11,14–16].

Exhaustive calculations of the ground state energies of different atoms within the HF approach and that based on the density functional corresponding to the HF approximation (DHF) have shown that there exists an inequality,

$$E_{DHF} \geq E_{OEP} > E_{HF},$$  \hspace{1cm} (1)

where $E_{DHF}$ is the ground state energy calculated in DHF, using a KS model system with the exact same density as that of some given HF ground states [17–19]. Here $E_{OEP}$ denotes the energy from the optimized potential method (OPM) [17,20], and $E_{HF}$ denotes the HF ground state energy (see e.g. [17–19]). One can assume that inequality $E_{OEP} > E_{HF}$ results from the fact that $E_{OEP}$ is calculated with the restrictions associated with local potentials while calculations of $E_{HF}$ are in this sense unrestricted (see e.g. [21]). But such considerations could justify only the relation $E_{OEP} \geq E_{HF}$. For instance, if one applies this consideration to the functional of the KS kinetic energy $T_k[\rho]$ one would expect that $T_k[\rho] > T^{HF}_k[\rho]$. Quite surprisingly, one has instead $T^{HF}_k[\rho] \geq T_k[\rho]$ (see e.g. [17]). Here $T^{HF}_k[\rho]$ is the HF functional of the kinetic energy. Then, one could expect, however, that instead the following relation holds (see, e.g. [18])

$$E_{DHF} = E_{OEP} = E_{HF},$$  \hspace{1cm} (2)

since a universal Hohenberg-Kohn (HK) functional is defined for HF ground states because of the constrained-search derivation [22]. Note, that this procedure also does not define explicitly the HF functional $F^{HF}[\rho]$ whose minimization leads to the HF ground state. The obvious contradiction between inequality (1) and equality (2) casts doubts on the reliability of the KS scheme and probably points to the possible contradictions in DFT based on the suggestion that an exact local exchange potential does not exist for ground states of typical atoms (see [18,19] and references therein). To solve the problem, we have to clarify the relationships between the HF exchange and kinetic functionals and the corresponding exchange and kinetic functionals of the DFT.

Without resorting to a numerical analysis, by clarifying the relationship between the nonlocal exchange HF potential and the local exchange KS potential, we show that inequality (1) and equality (2) have to be replaced by the inequality

$$E_{OEP} \geq E_{DHF} = E_{HF},$$  \hspace{1cm} (3)

We also consider the important problem of how to relate the single particle spectrum of a many electron system to the corresponding KS eigenvalues. This consideration enables us to clarify the relationship between the single particle spectra obtained in HF calculations and in the KS calculations.

The structure of the paper is the following. In Section II, for the reader’s convenience we review the main features of the HF method. We list only the main peculiarities of the HF method, which are directly determined by the nonlocal HF potential. One cannot expect to reproduce these within the Kohn-Sham theory of DFT. The explanation of Eqs. (1), (2), and (3) presented in Section III
consists in demonstrating that the contradictions come from omitting the correlation energy, which is defined by the difference between the sum of the kinetic and exchange energies of a system considered within DFT and HF approaches, respectively. Consequently, this difference, which has to be treated as a correlation energy $F_{cHF}[\rho]$, gives rise to a specific correlation energy, because the nonlocal HF potential ensures the deeper minimum value of the ground state energy than the local potential of OPM. We also clarify the relationships between HF exchange and kinetic functionals and the corresponding exchange and kinetic functionals of the DFT. Our consideration also shows that this correlation energy $F_{cHF}[\rho]$, being the specific feature of a finite system, cannot be represented by the local density approximation based on calculations of a homogeneous electron system. Therefore, the correlation energy of a finite electron system, which has to include $F_{cHF}[\rho]$, cannot be obtained from considerations of uniform electron systems, although this way to construct $E_c[\rho]$ is generally used [6]. In Section IV, we consider the single-particle excitation spectra of many-electron systems and relate them to the eigenvalues of the corresponding KS equations. We show that the single-particle spectra do not coincide with the eigenvalues of the KS or HF equations. A possible inconsistency in the Kohn-Sham theory based on calculations of the single-particle spectra [18,19] is also clarified in this Section. Finally, Section V contains our concluding remarks.

II. THE HARTREE-FOCK METHOD

Hartree’s equations, as Fock’s generalization of them, were derived for any atom with two and more electrons. In fact, they are applicable to any many-electron system in a static external potential $v(r)$. Assuming that the total electron wave function $\Psi(r_1,...r_N)$ can be approximated as a product of one-particle functions $\phi_i^H(r)$, $\Psi^H(r_1,...r_N) = \prod_{i=1}^{N} \phi_i^H(r_i)$, Hartree suggested [1] the following equation for $\phi_i^H(r)$:

$$
\left[ \frac{-\Delta}{2} + v(r) + \sum_{j=1, j\neq i}^{N} \frac{|\phi_j^H(r')|^2}{|r - r'|} \right] \phi_i^H(r) = E_i^H \phi_i^H(r). \tag{4}
$$

Here $N$ is the total number of electrons. For an atom one has $v(r) = -Z/r$, where $Z$ is the nuclear charge. An electron in an $i$-state is under the action of the so-called self-consistent field, which is determined by all electrons but the $i$th one. Excluding the term $j = i$ from the sum in (4) eliminates the action of the $i$-electron upon itself. In Hartree approximation the system’s electron density $\rho^H(r)$ is determined by the relation

$$
\rho^H(r) = \sum_{j=1}^{N} n_i |\phi_j^H(r)|^2,
$$

where $n_i$ are the occupation numbers.

Hartree’s approach has two obvious shortcomings: the total wave-function violates the exclusion principle and, since the self-consistent potential acting upon the $i$th electron depends upon $i$, the

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1 Atomic system of units is used in this paper: $e = m = \hbar = 1$, where $e$ and $m$ are electron charge and mass, respectively.
functions $\phi^H_i(r)$ are non-orthogonal. These shortcomings were eliminated in [2] by constructing the total wave function as an *anti-symmetrized* ($A$) product,

$$\Psi^{HF}(r_1, \ldots r_N) = A \prod_{j=1}^{N} \phi_i^{HF}(r_i),$$

which automatically satisfies the exclusion principle. This wave-function’s choice leads to the following ground state energy $E_{HF}$

$$E_{HF} = -\frac{1}{2} \sum_{j=1}^{N} n_j \int \phi_j^*(r) \nabla^2 \phi_j(r) dr + \frac{1}{2} \sum_{j=1, i=1}^{N} n_j n_i \int \frac{\phi_j^*(r_1) \phi_i^*(r_2) \phi_j(r_1) \phi_i(r_2)}{|r_1 - r_2|} dr_1 dr_2$$

$$- \frac{1}{2} \sum_{j=1, i=1}^{N} n_j n_i \int \frac{\phi_j^*(r_1) \phi_i^*(r_2) \phi_i(r_1) \phi_j(r_2)}{|r_1 - r_2|} dr_1 dr_2 + \sum_{j=1}^{N} \int \phi_j^*(r) \phi_j(r) v(r) dr,$$

and HF system of equations:

$$\hat{H}^{HF} \phi_i^{HF}(r) = \left[ -\frac{\Delta}{2} + v(r) \right] \phi_i^{HF}(r)$$

$$+ \sum_{j=1}^{N} \int \frac{dr'}{|r - r'|} \left[ |\phi_j^{HF}(r')|^2 \phi_i^{HF}(r) - \phi_j^{HF^*}(r') \phi_i^{HF}(r) \phi_j^{HF^*}(r) \phi_i^{HF}(r) \right] = E_i^{HF} \phi_i^{HF}(r).$$

These equations differ from an ordinary Schrödinger equation in two essential aspects: they are non-linear in $\phi_i^{HF}(r)$ and the second term under the sum that represents the so-called Fock’s potential is non-local.

The non-linearity of Hartree and HF equations leads to non-uniqueness of their solutions (see [23] and references therein): in some cases, a given energy value can be represented by more than one set of solutions which deliver this value with high numerical accuracy. Furthermore, the nonlocal HF potential leads to a number of very specific features of the ground state wave function, which cannot be reproduced by the KS equations, see Sec. III.

1. The asymptotic behavior in $r$ of $\phi_i^{HF}(r)$, contrary to the case of an ordinary one-particle Schrödinger and also Hartree equations, is not determined by $E_i^{HF}$ and does not behave as

$$\phi_i(r)|_{r \to \infty} \sim \exp(-\sqrt{2|E_i^{HF}|r}).$$

On the contrary, it was shown in [24] that at $r \to \infty$ the function $\phi_i^{HF}(r)$ is not determined by $E_i^{HF}$ but is of the form

$$\phi_i^{HF}(r)|_{r \to \infty} \sim \sum_l C_l \exp(-\sqrt{2|E_F^{HF}|r}) r^{l+1},$$

where $E_F^{HF}$ is the energy of the so-called Fermi-level (with wave function $\phi_F^{HF}(r)$), which is the smallest binding energy among all $E_i$ in the considered system, and

$$C_l = \sum_{m=-l}^{l} \int \phi_F^{HF^*}(r) r^m Y_{lm}(r/r) \phi_i^{HF}(r) dr.$$
Here $Y_{lm}(r/r)$ is the $l^{th}$ order spherical polynomial. The alteration of the asymptotic behavior dramatically affects, for example, the probability of penetration of atomic electrons via a potential barrier created when a strong electric static field is applied to this atom [25].

2. The number of zeroes in the radial part of the function $\phi_i^{HF}(r)$ is not equal, according to [26] and contrary to the case of an ordinary one-particle Schrödinger and also Hartree equations, to the so-called radial quantum number $n_r = n - l - 1$, where $n$ is the principal and $l$ is the angular momentum quantum numbers. The extra zeroes are located at big distances and their presence can be explained qualitatively in the following way. At large distances $\phi_i^{HF}(r)$ is determined mainly by the admixture of $\phi_i^{HF}(r)$ to $\phi_i^{HF}(r)$. The latter function adds its remote zeroes to that of $\phi_i^{HF}(r)$.

3. In the presence of the HF potential the electron velocity operator $\hat{v}$, which in quantum mechanics is determined by the relation $\hat{v} = i[\hat{H}^{HF}, r]$, is not equal to $\hat{p}$ (note, that $m = 1$), contrary to the case of a local potential. This drastically affects, for example, the photoionization cross section calculations: the amplitude of this process becomes different in the so-called "length" and "velocity" forms and the golden sum rule is violated [3]. It is of interest to note that this violation is very serious and can be eliminated only when the corresponding calculations are performed within RPAE framework.

4. One-electron Green’s function $G^{HF}_{E}(r_1, r_2)$ in HF has only one expression via $\phi_i^{HF}(r)$, namely

$$G^{HF}_{E}(r_1, r_2) = \sum_i \frac{\phi^{HF\ast}_i(r_1)\phi^{HF}_i(r_2)}{E_i - E + i\delta},$$

while in case of the spherical symmetry there exist two equivalent expressions for local potentials

$$G_{E}(r_1, r_2) = \sum_i \frac{\phi^\ast_i(r_1)\phi_i(r_2)}{E_i - E + i\delta} = \phi^\ast_{E}(r_{<})\chi_{E}(r_{>}),$$

where $r_{>(<)}$ is the larger (smaller) value of $r_{1,2}$ and $\chi_{E}(r_{>})$ is the solution of the same Schrödinger (and also Hartree) equation as $\phi^\ast_{E}(r_{<})$, but irregular at $r = 0$. Note, that $\phi_{E}(r)$ is regular at $r \to 0$.

5. Another specific feature of the HF potential is the behavior as a function of the incoming electron energy $E$ of elastic scattering phase shifts $\delta_l(E)$ of a partial wave with angular momentum $l$. As is well known, if the wave function’s phase of electron scattering upon a local potential $v(r)$ is normalized in such a way that $\delta_l(E)|_{E \to \infty} \to 0$, the relation $\delta_l(0) = q_l\pi$ holds, where $q_l$ is the number of the electron’s "vacant" bound states with angular momentum $l$ in this potential (see e.g. [27]). The situation for the HF potential is qualitatively different. With the same normalization $\delta_l^{HF}(E)|_{E \to \infty} \to 0$ another relation holds: $\delta_l^{HF}(0) = (q_l + t_l)\pi$, where $t_l$ is the number of "occupied" bound states with angular momentum $l$ in the HF potential [3,23].

III. THE KS LOCAL EXCHANGE POTENTIAL AND THE HARTREE-FOCK NONLOCAL ONE

Consider a many-body system composed of $N$ interacting electrons and moving in an external potential $v(r)$, with Hamiltonians $\hat{H}$ and $\hat{H}_v$ that are of the form

$$\hat{H} = \hat{T} + \hat{U},$$

and
\[ \hat{H}_v = \hat{T} + \hat{U} + \hat{V}. \]  

Here \( \hat{T} \), \( \hat{U} \), and \( \hat{V} \) are given in terms of the field operators \( \hat{\psi} (\mathbf{r}) \), and \( \hat{T} \) is the kinetic energy operator 

\[ \hat{T} = -\frac{1}{2} \int \hat{\psi}^*(\mathbf{r}) \nabla^2 \hat{\psi}(\mathbf{r}) d\mathbf{r}, \]  

\( \hat{U} \) is the interelectron interaction energy operator 

\[ \hat{U} = \frac{1}{2} \int \frac{\hat{\psi}^*(\mathbf{r}_1) \hat{\psi}^*(\mathbf{r}_2) \hat{\psi}(\mathbf{r}_2) \hat{\psi}(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2, \]  

and \( \hat{V} \) is the potential energy operator in the field \( v(\mathbf{r}) \) 

\[ \hat{V} = \int \hat{\psi}^*(\mathbf{r}) \hat{\psi}(\mathbf{r}) v(\mathbf{r}) d\mathbf{r}. \]  

Hohenberg and Kohn proved that there exists a one-to-one correspondence between \( v(\mathbf{r}) \) and the single-electron density \( \rho(\mathbf{r}) \), that is \( v(\mathbf{r}) \) is a unique functional of the density, apart from an additive constant [4]. Because \( v(\mathbf{r}) \) fixes the Hamiltonian Eq. (13), the ground state wave function \( \Psi_0 \) is a functional of the density, and one can define the energy functional [4]

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

with \( F[\rho] \) being a universal functional independent of the number of particles \( N \) and the external potential \( v(\mathbf{r}) \). Note that the functional \( F[\rho] \) can also be obtained on the basis of the constrained-search derivation of Levy, when it is defined by the minimum over the set of all normalized \( N \)-electron wave functions \( \Psi_s \) that determine the density \( \rho(\mathbf{r}) \) [22]

\[ F[\rho] = \min \left( \Psi_s | \hat{T} + \hat{U} | \Psi_s \right). \]  

Provided the density is exact, \( \rho(\mathbf{r}) = \rho_0(\mathbf{r}) \), and normalized by the number of particles \( N \), \( N = \int \rho(\mathbf{r}) d\mathbf{r} \), the functional \( E[\rho] \) assumes its minimum value that is equal to the ground state energy \( E_0 \)

\[ E_0 = F[\rho_0] + \int v(\mathbf{r}) \rho_0(\mathbf{r}) d\mathbf{r}. \]  

Here the ground state density \( \rho_0(\mathbf{r}) \) is determined by the equation

\[ \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} + v(\mathbf{r}) = \mu, \]  

and \( \mu \) is the so-called chemical potential. The number \( \mu \) ensures the conservation of the number of particles \( N \). It is clear that if \( \hat{U} = 0 \), [see Eq. (13)], the functional \( F[\rho] \) reduces to the functional \( T_k[\rho] \) of the kinetic energy of noninteracting particles.

Equation (20) can be replaced by a set of Hartree-like single-particle equations [see Eq. (4)], which permits the calculation of the density \( \rho(\mathbf{r}) \) [5].
\[
\left( -\frac{\Delta}{2} + V_L(r) \right) \phi_i(r) = \varepsilon_i \phi_i(r),
\]

(21)

with the potential \( V_L = V_H + V_{xc} + v \). The density \( \rho(r) \) is given by

\[
\rho(r) = \sum_i n_i |\phi_i(r)|^2.
\]

(22)

Here \( V_H \) is the Hartree potential [see Eq. (4)],

\[
V_H(r) = \frac{\delta}{\delta \rho(r)} F_H = \int \frac{\rho(r_1)}{|r - r_1|} dr_1,
\]

(23)

where \( F_H \) is the Hartree functional

\[
F_H = \frac{1}{2} \int \frac{\rho(r_1) \rho(r_2)}{|r - r_1|} dr_1 dr_2,
\]

(24)

and the exchange-correlation potential, \( V_{xc}(r) = \delta F_{xc}/\delta \rho(r) \), is obtained from the exchange-correlation functional,

\[
F_{xc}[\rho] = F[\rho] - T_K[\rho] - F_H[\rho].
\]

(25)

In the same way, it is possible to define separately \( F_x \) and the correlation functional \( F_c \) using the equation, which can be considered as a definition of \( F_c \) [5]

\[
F_c[\rho] = F_{xc}[\rho] - F_x[\rho].
\]

(26)

Here \( F_x[\rho] \) is the exchange functional [10,28]

\[
F_x[\rho] = -\frac{1}{2} \int \frac{\chi_0(r_1, r_2, iw) + 2\pi \rho(r_1) \delta(w) \delta(r_1 - r_2) dw}{|r_1 - r_2|} 2\pi dr_1 dr_2
\]

\[
= -\sum_{k,i} n_k n_i \int \left[ \frac{\phi_i^*(r_1) \phi_i(r_2) \phi_k^*(r_2) \phi_k(r_1)}{|r_1 - r_2|} \right] dr_1 dr_2,
\]

(27)

and \( \chi_0 \) is the linear response function, which is of the form

\[
\chi_0(r_1, r_2, \omega) = \sum_{i,k} n_i (1 - n_k) \phi_i^*(r_1) \phi_i(r_2) \phi_k^*(r_2) \phi_k(r_1) \left[ \frac{1}{\omega - \omega_{ik} + i\eta} - \frac{1}{\omega + \omega_{ik} - i\eta} \right],
\]

(28)

with \( \omega_{ik} \) defined as \( \omega_{ik} = \varepsilon_k - \varepsilon_i \), \( \varepsilon_k \) and functions \( \phi_k(r_1) \) being respectively the one-particle energies and wave functions of Eq. (21); \( \eta \to 0 \). Having the functional \( F_x \) given by Eq. (27), we can construct the HF-like scheme based on Eq. (21) with the local KS exchange potential [10,28]

\[
V_x(r) = \frac{\delta}{\delta \rho(r)} F_x[\rho].
\]

(29)

The functional of density \( F_{KS}^{x} \) corresponding to the HF approximation can be defined as follows
that there is a one-to-one correspondence between the HF functional of the exchange energy and then the HF functional of the exchange energy state wave function \( E \) and the eigenvalues \( T \) and the eigenvalues \( E \) and the eigenvalues \( \epsilon \). Note that examples of densities which are not representable were given in Ref. \([29]\). Obviously, a

\[
F_{r}^{KS}[\rho] = T_{k}[\rho] + F_{H}[\rho] + F_{x}[\rho].
\]

In fact, this functional is determined by the value of \( F_{r}^{KS}[\rho] = (\Phi^{KS}|H|\Phi^{KS}) \), if \( \Phi^{KS} \) is a single \( N \)-electron Slater determinant which delivers the lowest energy expectation value of \( H \) given by Eq. (12) and yielding the density \( \rho(\mathbf{r}) \). This determinant is composed of the single-particle wave functions, which are solutions of a single-particle equation like Eq. (21) provided that \( V_{L}(\mathbf{r}) \) is a local potential. We denote this determinant by \( \Psi^{KS}[\rho] \). On the other hand, the same wave function in the frame of the optimized effective potential [20] is determined by the local exchange potential \( V_{OPM} \). Because of the one-to-one correspondence between this wave function and the local single-particle potential [4] we can conclude that \( V_{OPM} \) coincides with \( V_{x} \) given by Eq. (29). This result is in accord with the direct comparison of \( V_{x} \) with \( V_{OPM} \) that confirms their equality, \( V_{x}(\mathbf{r}) = V_{OPM}(\mathbf{r}) \) \([10,28]\). Therefore, the ground state energy \( E_{OEP} \) of a many-electron system calculated in OPM has to be equal to the corresponding energy calculated with the functional given by Eq. (30), \( E_{KSX} \), that is \( E_{KSX} = E_{OEP} \).

Now we turn to the HF calculations based on the constrained-search formulation of DFT, which leads to the HF functional \( F_{HF}[\rho] \) \([22]\). As it was mentioned in Section II and in accord with the constrained-search formulation \([22]\), the HF functional is determined by the minimum of the expectation value \( F_{HF}[\rho] = (\Psi[\rho]|\hat{H}|\Psi[\rho]) \) when the minimization runs over all single-electron Slater determinants yielding the density \( \rho(\mathbf{r}) \). The determinant, which yields the minimum value, is denoted as \( \Psi_{HF}[\rho] \). This construction of the functional \( F_{HF}[\rho] \) makes it clear that the ground state energy \( E_{DHF} \) of an electron system calculated with \( F_{HF}[\rho] \) is equal to \( E_{HF} \). Note that the determinant \( \Psi_{HF}[\rho] \) is composed of the eigenfunctions of Eq. (6) incorporating the Fock nonlocal potential. As a result, we can at first define the HF functional of the kinetic energy

\[
T_{k}^{HF}[\rho] = \left( \Psi_{HF}[\rho]|\hat{T}|\Psi_{HF}[\rho] \right),
\]

and then the HF functional of the exchange energy

\[
F_{x}^{HF}[\rho] = \left( \Psi_{HF}[\rho]|\hat{U}|\Psi_{HF}[\rho] \right) - F_{H}[\rho].
\]

We will now show that \( T_{k}^{HF}[\rho] \neq T_{k}[\rho] \), and our proof proceeds by \textit{reductio ad absurdum}. Note that there is a one-to-one correspondence between \( \rho(\mathbf{r}) \), the single-particle potential and the ground state wave function [4]. Because \( T_{k}[\rho] \) is a unique functional of the density, each value of \( T_{k}[\rho] \) fixes the only ground state function. This function is a single Slater determinant \( \Phi^{KS} \) yielding the density \( \rho(\mathbf{r}) \) normalized to \( N \) electrons and characterized by the single-particle wave functions \( \phi_{i} \) and eigenvalues \( \epsilon_{i} \), given by Eq. (21). Assume that \( T_{k}^{HF}[\rho] = T_{k}[\rho] \). Then the HF wave functions \( \Psi^{HF}[\rho] \) and the eigenvalues \( E_{i}^{HF} \) given by Eq. (6) must be equal to \( \Phi^{KS}[\rho] \) and the eigenvalues \( \epsilon_{i} \) given by Eq. (21). As it was mentioned in Sec. II, Eq. (8), all of the HF single-particle functions have the same long-range behavior which is dominated by the smallest orbital energy [24], while, generally speaking, the eigenvalues \( E_{i}^{HF} \) are not degenerate. On the other hand, eigenfunctions of Eq. (21) can have such a behavior only if the eigenvalues \( \epsilon_{i} \) are degenerate. In order to eliminate the contradiction we have to recognize that \( T_{k}^{HF}[\rho] \neq T_{k}[\rho] \), and some of densities, which are the ground state densities of single-particle Schrödinger equations with nonlocal potentials are not noninteracting \( v \) representable in the sense that they cannot be the ground state density of Eq. (21) with some local potential \( v(\mathbf{r}) \).
one-to-one correspondence between nonlocal potentials and local ones does not exist [30]. Therefore,
if we would even have the functional $F^{HF}[\rho]$ explicitly we would not have been able to calculate the
HF ground state within the KS theory because the HF ground state cannot be reproduced by Eq.
(21) with a local single-particle potential. On the other hand, the HF ground state can be obtained
by solving the Hohenberg-Kohn equation (20) with $F[\rho] = F^{HF}[\rho]$. These facts do not imply any
contradictions. The Kohn-Sham theory and Eq. (20) lead to the same result if the density $\rho(r)$
of system under consideration is $v$ representable. Otherwise one has to use Eq. (20). A detailed
investigation of this important problem will be published elsewhere.

The functional $T_k^{HF}$ given by Eq. (31) is determined in the domain of the HF densities $\rho_{HF}$
generated by the non-local Fock potential entering Eq. (6), while $T_k$ is determined in the domain of
the densities $\rho_L$ given by Eq. (21). Note that both of the densities are normalized to same number of
electrons. Approximating $\rho_{HF}$ by $\rho_L$, one has to obtain $T_k < T_k^{HF}$ because of the minimum principle
which ensures that the Slater determinant $\Phi^{KS}$ delivers the minimum value of the kinetic energy
$T_k$. This result is confirmed by numerical calculations [17]. On the other hand, due to the minimum
principle $F^{HF} < F_x^{KS}$. Following Ref. [17], we can define the HF exchange-correlation functional
$F_{xc}^{HF}[\rho]$

$$F_{xc}^{HF} = F_x^{HF} - T_k - F_H = T_k^{HF} + F_x^{HF} - T_k,$$  \hspace{1cm} (33)

and introduce the HF correlation functional $F_c^{HF}$

$$F_c^{HF} = F_{xc}^{HF} - F_x = T_k^{HF} + F_x^{HF} - T_k - F_x.$$  \hspace{1cm} (34)

We note that Eqs. (33) and (34) cannot be considered as exact definitions of $F_{xc}^{HF}$ and $F_c^{HF}$ because it
is impossible to approximate exactly $\rho_{HF}$ by $\rho_L$. It follows from Eq. (34) that the correlation energy
$F_c^{HF}$ exists. This energy must be taken into account when constructing constructing approximations
of $F^{HF}$ within the KS framework. Omitting $F_c^{HF}$, one obtains Eq. (1), while properly constructing
$F^{HF}[\rho]$ based on the constrained-search formulation of DFT [22], one obtains Eq. (3) rather then Eq. (2).

In the case of He atoms the HF potential acting on the occupied states is a local potential.
Therefore, the kinetic energy functional $T_k^{HF}[\rho]$ coincides with $T_k[\rho]$ leading to the equality $F_x^{HF}[\rho] = F_x^{KS}[\rho]$, and $E_{OEP} = E_{DHF} = E_{HF}$ in line with Eqs. (2) and (3). This observation is confirmed by
numerical calculations [18]. For all other atoms, the HF potential is nonlocal, and $F_c^{HF}[\rho]$ contributes
to the ground state energy. Obviously, one has $E_{OEP} \geq E_{DHF} = E_{HF}$ in accordance with Eq. (3)
and the numerical calculations [18]. In the case of a homogeneous system, both single-particle wave
functions, $\phi_i^{HF}(r)$ given by Eq. (6) and the ones $\phi_i(r)$ given by Eq. (21), are plane waves. As a result,
the energy $E_{KSX} = E_{HF}$ (though the Fock potential, Eq. (6), is a nonlocal) and the correlation energy
$E_c = E - E_{KSX} = E - E_{HF}$ is uniquely defined. This consideration shows that $F_c^{HF}[\rho]$, being the
specific feature of a finite system, cannot be approximated by the local density approximation based
on calculations of a homogeneous electron system. Thus, $E_c[\rho]$ of a finite electron system, which has
to include $F_c^{HF}[\rho]$, cannot be obtained from considerations of uniform electron systems, although
this way to construct $E_c[\rho]$ is generally used [6]. As a result, we are led to the conclusion that the HF
method has unique peculiarities which can be considered as useful rather then as shortcomings when
investigating many-electron systems. Moreover, it is of great importance to check in experiments
whether the wave function of a real physical system has the behavior resembling the behavior of
the HF wave function given by Eq. (8) because this point is closely related to the problem of the \(\nu\)-representability. As mentioned in Sec. II, this HF-like behavior can be checked measuring the probability of penetration of atomic electrons via a potential barrier [25].

**IV. SINGLE PARTICLE SPECTRA**

In order to calculate the single-particle energies \(\epsilon_i\) of a many-electron system we have to consider the ground state energy as a functional of the density \(\rho\) and of the occupation numbers \(n_i\). The occupation numbers are widely used in generalizations of DFT when extending DFT to finite temperatures, when considering excitations energies and so on, for a short review see Ref. [29,31]. Taking into account \(n_i\), we can use the well-known Landau equation of the Fermi liquid theory [32]

\[
\frac{\delta E}{\delta n_i} = \epsilon_i. \tag{35}
\]

We note that there exist close relations between the Fermi-liquid theory and DFT [11], while the Fermi-liquid theory is applicable in principle essentially to all types of Fermi systems including finite objects such as atoms, molecules, clusters and fullerenes. It is difficult to provide an example of a Fermi system, which cannot at all be described in the frame of this theory (see e.g. [32,33]).

In the functional \(E[\rho, n_i]\) both of the parameters, \(\rho\) and \(n_i\), are independent variables and determine different features of the system under consideration. The ground state energy as a functional of the density determines the system’s behavior in an external field, while the ground state energy as a functional of the occupation numbers characterizes the single-particle spectrum. On the other hand, the functional \(F[\rho]\) given by Eq. (18) depends only on the density. One can use some approximations to construct \(E[\rho, n_i]\). For instance, writing the density in explicit form given by Eq. (22), we find that the functional \(F[\rho]\) depends upon the occupation numbers \(n_i\) [18,19,34]

\[
F[\rho, n_i] \equiv F \left[ \sum n_i |\phi_i(r)|^2 \right], \tag{36}
\]

while \(E[\rho, n_i]\) is given by Eq. (17). In that case, using Eq. (35) one can show that the single-particle energies \(\epsilon_i\) coincide with the eigenvalues \(\epsilon_i\) of Eq. (21) [34].

Let us show that the procedure based on Eq. (36) may lead, however, to wrong results. Consider a large uniform system of fermions, so that it is possible to introduce the density of states at the Fermi-level. In this case, the single-particle potential is a constant, the eigenvalues of Eq. (21) are the eigenvalues of noninteracting fermions with bare mass \(M\), and the density of states is equal to that of noninteracting fermions. This result is incorrect being related to the fact that the functional form \(E[\rho, n_i]\) given by Eq. (36) was artificially chosen. In contrast, as it is seen from Eq. (5), the HF ground state energy depends on the occupation numbers quite naturally and leads to the correct results when calculating the single-particle spectra [32,35,36]. Inserting Eq. (5) into Eq. (35), we can calculate the HF single-particle spectrum \(\epsilon_i^{HF}\) that coincides with the eigenvalues of Eq. (6). In case of a large uniform system of electrons, one can check that the density of states tends to zero [35,36]. Upon comparing this result with the result of the KS scheme, one may suspect an inconsistency in the KS approach. An inconsistency like this was indeed suspected in KS approach because \(\sum n_i \epsilon_i \neq \sum n_i E_i^{HF}\) [18,19], with \(\epsilon_i\) being calculated in the scheme of [34].
In order to show that the inconsistencies mentioned above are fictitious and to illustrate how to calculate the single-particle energies \( \epsilon_i \) within the DFT, we choose the simplest case when the functional is given by Eq. (30). As we shall see, the single-particle energies \( \epsilon_i \) coincide neither with the eigenvalues \( E_{HF}^i \) of Eq. (6) nor with \( \epsilon_i \) of Eq. (21). To proceed, we use a method developed in [15,28,37,38]. The linear response functions \( \chi_0 \), and the density \( \rho(r) \) depend upon the occupation numbers. Thus, one can consider the ground state energy as a functional of the density and the occupation numbers

\[
E[ho(r), n_i] = T_k[\rho(r), n_i] + F_H[\rho(r), n_i] + F_x[\rho(r), n_i] + \int V_{\text{ext}}(r)\rho(r) dr. \tag{37}
\]

Here \( T_k \) is the functional of the kinetic energy of noninteracting KS particles. Substituting Eq. (37) into Eq. (35) and remembering that the single-particle wave functions and eigenvalues are given by Eq. (21), we see that the single particle spectrum \( \epsilon_i \) can be represented by the following expression:

\[
\epsilon_i = \epsilon_i - \langle \phi_i | V_x | \phi_i \rangle - \frac{1}{2} \delta \frac{\delta n_i}{n_i} \int \left| \frac{\chi_0(r_1, r_2, iw) + 2\pi\rho(r_1)\delta(w)\delta(r_1 - r_2)}{|r_1 - r_2|} \right| dw dr_1 dr_2. \tag{38}
\]

The first and second terms on the right hand side in Eq. (38) are determined by the derivative of the functional \( T_k \) with respect to the occupation numbers \( n_i \). To calculate the derivative we consider an auxiliary system of non-interacting particles in a field \( U(r) \). The ground state energy \( E_0^U \) of this system is given by the following equation

\[
E_0^U = T_k + \int U(r)\rho(r) dr. \tag{39}
\]

Varying \( E_0^U \) with respect to the occupation numbers, one gets the desirable result

\[
\epsilon_i = \frac{\delta E_0^U}{\delta n_i} = \frac{\delta T_k}{\delta n_i} + \langle \phi_i | U | \phi_i \rangle, \tag{40}
\]

provided \( U = V_H + V_x + v \). The third term on the right hand side of Eq. (38) is related to the contribution coming from \( F_x \) defined by Eq. (27). In the considered simplest case when we take into account only \( T_k \), \( F_H \) and \( F_x \) functionals, the infraction enters as a linear factor, with \( F_H \) and \( F_x \) being linear dependent on the strength. If we omit the inter-electron interaction given by Eq. (15) we directly get from Eq. (37) \( \epsilon_i = \epsilon_i \) as it must be in the case of noninteracting system of electrons. Note that it is not difficult to include the correlation energy in the simplest local density approximation

\[
F_c[\rho, n_i] = \int \rho(r)\epsilon_c(\rho(r)) dr. \tag{41}
\]

Here the density \( \rho(r) \) is given by Eq. (22) and the correlation potential is defined as

\[
V_c(r) = \frac{\delta F_c[\rho]}{\delta \rho(r)}. \tag{42}
\]

Then Eq. (37) takes the form
\[ E[\rho(r), n_i] = T_k[\rho(r), n_i] + F_H[\rho(r), n_i] + F_x[\rho(r), n_i] + F_c[\rho(r), n_i] + \int V_{\text{ext}}(r)\rho(r)dr. \] (43)

Varying \( E[\rho(r), n_i] \) with respect to the occupation numbers \( n_i \) and after some straightforward calculations, we obtain the rather simple expression for the single particle spectrum

\[ \epsilon_i = \varepsilon_i - <\phi_i|V_x|\phi_i> - \sum_k n_k \int \left[ \frac{\phi_i^+(r_1)\phi_i(r_2)\phi_k^+(r_1)\phi_k(r_2)}{|r_1 - r_2|} \right] dr_1 dr_2. \] (44)

Here we employ Eq. (40) and choose the potential \( U \) as \( U = V_H + V_x + V_c + v \) to calculate the derivative \( \delta T_k/\delta n_i \). Approximating the correlation functional \( F_c[\rho, n_i] \) by Eq. (41) we simplify the calculations a lot, preserving at the same time the asymptotic condition, \( (V_x + V_c)_{r\to\infty} \to -1/r \). This condition is of crucial importance when calculating the wave functions and eigenvalues of vacant states in the frame of the KS approach [28,37]. Note, that these functions and eigenvalues that enter Eq. (44) determine the single particle spectrum \( \epsilon_i \). This spectrum has to be compared with the experimental results.

Single particle levels \( \epsilon_i \) given by Eq. (44) resemble the ones that are obtained using HF method. If the wave functions \( \phi_i \) were solutions of the HF equations, the correlation potential \( V_c \) would be omitted, then the energies \( \epsilon_i \) would exactly coincide with the eigenvalues \( \varepsilon_i \). But this is not the case, since \( \phi_i \) and \( \varepsilon_i \) are the eigenfunctions and eigenvalues of Eq. (21). Therefore, the energies \( \epsilon_i \) coincide neither with HF eigenvalues given by Eq. (6), nor with the ones of Eq. (21). As we have seen in Section III, in case of the He atom \( T_k^{HF}[\rho] = T_k[\rho] \) and \( F_x^{HF}[\rho] = F_x^{KS}[\rho] \). Then it follows from Eq. (44) that \( \sum_i n_i \epsilon_i = \sum_i n_i T_k^{HF} = \sum_i n_i \varepsilon_i \) in accordance with numerical results obtained in [18]. In case of other atoms we cannot expect this equality to hold because of the non-locality of the HF single-particle potential. This result is in agreement with the numerical calculations [18,19] and has nothing to do with contradictions between the HF method and DFT.

It is worth noting that if the exchange functional \( F_x[\rho] \) is treated within the local density approximation, as it is done for \( F_c[\rho] \), that is one uses Eq. (36) to construct \( E[\rho, n_i] \), then the second and the third terms on the right hand side of Eq. (44) cancel each other, leading to \( \epsilon_i = \varepsilon_i \) in accordance with [34]. Therefore it is of crucial importance to keep the proper representation of the functional \( F_x[\rho] \) given by Eq. (27). We also anticipate that Eq. (44) when applied to calculations of many-electron systems such as atoms and molecules will produce reasonable results for the energy gap separating the occupied and empty states. In case of solids, we expect that the energy gap at various high-symmetry points in the Brillouin zone of semiconductors and dielectrics can also be reproduced.

**V. CONCLUDING REMARKS**

We have shown that there are no contradictions in DFT related to the fact that the HF-like calculations of finite electron systems carried out within the Kohn-Sham theory of DFT lead to the ground state energy, the absolute value of which is smaller than that calculated within the HF method. On the other hand, we have demonstrated that the properly constructed HF functional of the density produces the ground state energy, which coincides with the energy obtained within HF calculations. While inequalities (1) and (2) came from omitting the correlation energy, which is defined by the difference between the sum of the kinetic and exchange energies of a system considered within the
KS approach and the HF method, respectively. It is the nonlocal exchange potential entering the HF equations that generates this correlation energy. We have shown that this functional $F_c^{HF}$ of the correlation energy, being the specific feature of a finite system, cannot be approximated by the local density approximation based on calculations of a homogeneous electron system. Thus, the correlation energy of a finite electron system, which has to include $F_c^{HF}[\rho]$, cannot be obtained from considerations of uniform electron systems, although this way of constructing $E_c[\rho]$ is generally used. We can conclude that the HF method has unique peculiarities which can be useful when investigating many-electron systems.

We have clarified the relationship between the eigenvalues of the single-particle KS equations, the HF eigenvalues and the real single-particle spectrum. Again, there are no contradictions based on the comparison of the single-particle spectra calculated within DFT and the HF method. We have presented a simple equation defining the single-particle spectrum of a many-electron system. It is worth noting that all the specific features of the HF method mentioned in Section II are dictated by the HF nonlocal potential and therefore give no grounds to seek possible contradictions in the Kohn-Sham theory which deals with local single-particle potentials and $v$ representable densities. As it was mentioned in Section II, the HF method has some drawbacks. Among them there is a well-known consequence of the non-locality of the HF single-particle exchange potential, which leads to the fact that the HF single-particle potential acting on the unoccupied states falls of exponentially. As a result, the HF potential can support very few unoccupied states. Such a poor situation with the number of states develops difficulties in treating the excited states. By contrast, the KS theory does not suffer from the drawbacks of the HF method.

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