

# THE PROBLEM OF THE UNIVERSAL DENSITY FUNCTIONAL AND THE DENSITY MATRIX FUNCTIONAL THEORY

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The analysis in this paper shows that the Hohenberg–Kohn theorem is the constellation of two statements: i) the mathematically rigorous Hohenberg–Kohn lemma, which demonstrates that the same ground-state density cannot correspond to two different potentials of an external field, and ii) the hypothesis of the existence of the universal density functional. Based on the obtained explicit expression for the nonrelativistic particle energy in a local external field, we prove that the energy of the system of more than two noninteracting electrons cannot be a functional of the inhomogeneous density. This result is generalized to the system of interacting electrons. It means that the Hohenberg–Kohn lemma cannot provide justification of the universal density functional for fermions. At the same time, statements of the density functional theory remain valid when considering any number of noninteracting ground-state bosons due to the Bose condensation effect. In the framework of the density matrix functional theory, the hypothesis of the existence of the universal density matrix functional corresponds to the cases of noninteracting particles and to interaction in the Hartree–Fock approximation.

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## 1. INTRODUCTION

The main point of the Hohenberg–Kohn seminal paper [1], devoted to the justification of the density functional theory (DFT), is the statement that the external field potential “ $v(\mathbf{r})$  is (to within a constant) a unique functional of  $n(\mathbf{r})$ ”. The function  $n(\mathbf{r})$  is an inhomogeneous ground-state density of the electron gas placed in an external static field  $v(\mathbf{r})$ . On the ground of this statement, the second statement is formulated [1]: “since, in turn,  $v(\mathbf{r})$  fixes  $H$ , we see that the full many-particle ground state is a unique functional of  $v(\mathbf{r})$ ”, where  $H$  is the explicit Hamiltonian of the interacting electron system in the static external field  $v(\mathbf{r})$ . The second statement in quotes is trivial if the first one is true. Below, we show that the first

(and the main) statement that  $v(\mathbf{r})$  is a unique functional of  $n(\mathbf{r})$  is not equivalent to the statement, proved in [1], that the same inhomogeneous density  $n(\mathbf{r})$  cannot correspond to two different local potentials  $v_1(\mathbf{r})$  and  $v_2(\mathbf{r})$  of the external field in the ground state of the nonrelativistic system of electrons (except the case  $v_1(\mathbf{r}) - v_2(\mathbf{r}) = \text{const}$ ) [1, 2]. The last statement is rigorous and we call it the Hohenberg–Kohn lemma in what follows. Hence, the inhomogeneous density  $n(\mathbf{r})$  of the ground-state nonrelativistic electron system uniquely corresponds to the potential  $v(\mathbf{r})$  (to within an additive constant). In the case of ground state degeneration, the lemma relates to the density  $n(\mathbf{r})$  of any ground state. At the same time, the statement “ $v(\mathbf{r})$  is (to within a constant) a unique functional of  $n(\mathbf{r})$ ” is not true for the system of more than two interacting electrons (or, more general, Fermi particles).

According to the Hohenberg–Kohn paper [1], it follows from the statement of the lemma that the external field potential  $v(\mathbf{r})$  is an inhomogeneous density functional

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$$n(\mathbf{r}) = n(\mathbf{r}, [v]) \rightarrow v(\mathbf{r}) = v(\mathbf{r}, [n]) + \text{const}. \quad (1)$$

The existence of the functional (the square brackets in (1)) means that there is a universal rule according to which the value of the external field potential  $v(\mathbf{r})$  at each point  $\mathbf{r}$  can be found if the inhomogeneous density  $n(\mathbf{r})$  corresponding to the ground state of the system is known. This means that, in principle, there exists (although cannot be explicitly found or indicated) a rule for determining the function  $v(\mathbf{r})$  by the known function  $n(\mathbf{r})$  whose structure is independent of the explicit form of  $v(\mathbf{r})$  and  $n(\mathbf{r})$ . We emphasize that this very strong statement has not yet been called into question. In fact, in the general case, there is no one-to-one correspondence between the Hohenberg–Kohn lemma and relation (1) on a functional dependence. It only follows from the Hohenberg–Kohn lemma that quite a definite external field  $v(\mathbf{r})$  can be put in correspondence with each function  $n(\mathbf{r})$  (up to a constant factor). But this does not mean that such a correspondence is established by the unified rule  $v(\mathbf{r}) = v(\mathbf{r}, [n])$  universal for any external field [3].

In other words, each external field determines a unique density (it is clear, e.g., on the basis of the universal rules of the perturbation theory), and each density determines a unique external field on the basis of the Hohenberg–Kohn lemma. However, the rule for the last correspondence can be nonuniversal. This rule in general depends on the concrete form of the density. The possibility of such a nonuniversality of the rule of correspondence for the “inverse” functional  $v(\mathbf{r}) = v(\mathbf{r}, [n])$  was not considered in [1]. The existence of this nonuniversality violates the Hohenberg–Kohn theorem, although the Hohenberg–Kohn lemma is undoubtedly correct. Below, we show that the universal density functional does not exist in the case where the number of fermions is greater than two.

## 2. FORMULATION OF THE PROBLEM

For the reasons discussed in the Introduction, we note that the inhomogeneous density  $n(\mathbf{r})$  is a functional  $n(\mathbf{r}, [v])$  by definition,

$$n(\mathbf{r}) = \langle \Psi_0 | \Psi^\dagger(\mathbf{r}) \Psi(\mathbf{r}) | \Psi_0 \rangle.$$

The ground-state wave function  $\Psi_0$  is a functional of the external field  $v(\mathbf{r})$ ,  $\Psi_0 = \Psi_0[v]$ . Here,  $\Psi^\dagger(\mathbf{r})$  and  $\Psi(\mathbf{r})$  are the field creation and annihilation operators. This means that at each point, the inhomogeneous density is determined by the external field potential. Hence, the correspondence rule between the density

$n(\mathbf{r})$  and the field  $v(\mathbf{r})$  is established based on the solution of the corresponding Schrödinger equation for the wave function  $\Psi_0$  in a given external field  $v(\mathbf{r})$  and on finding the inhomogeneous density  $n(\mathbf{r})$ .

Then, it only follows from the lemma proved by Hohenberg and Kohn [1] that the functional  $n(\mathbf{r}, [v])$  is unique (taking the condition  $n(\mathbf{r}, [v]) = n(\mathbf{r}, [v + \text{const}])$  into account). It is clear that the functional  $n(\mathbf{r}, [v])$  is essentially nonlinear in the external field  $v(\mathbf{r})$ . This means that two possibilities are admissible without violating the Hohenberg–Kohn lemma: (i) the inverse problem of finding the dependence of  $v(\mathbf{r})$  on  $n(\mathbf{r})$  has individual solutions for each pair of functions  $n(\mathbf{r})$  and  $v(\mathbf{r})$  (or for certain types (classes) of pairs of functions  $n(\mathbf{r})$  and  $v(\mathbf{r})$ ); (ii) the inverse problem has a universal solution  $v(\mathbf{r}) = v(\mathbf{r}, [n])$ . As noted above, this dilemma is not usually considered, and it is assumed that there is the universal solution  $v(\mathbf{r}, [n])$  valid for any external field and any number of particles, i.e., possibility (ii) is always realized [3].

The essence of the problem under consideration can be expressed in other words. We introduce the operator  $P$  that establishes the relation between the functions  $n(\mathbf{r})$  and  $v(\mathbf{r})$ :

$$n(\mathbf{r}) = Pv(\mathbf{r}).$$

The operator  $P$  then provides the equality

$$Pv(\mathbf{r}) = P\{v(\mathbf{r}) + \text{const}\}.$$

In addition, it follows from the definition of the inhomogeneous density  $n(\mathbf{r})$  that the operator  $P$  is nonlinear. Therefore, the problem of finding the inverse operator  $P^{-1}$  that establishes the relation between  $v(\mathbf{r})$  and  $n(\mathbf{r})$ ,  $v(\mathbf{r}) = P^{-1}n(\mathbf{r})$ , has no unique solution. The difficulty is just in the nonlinearity of the relation between the functions  $n(\mathbf{r})$  and  $v(\mathbf{r})$ , otherwise the inverse operator  $P^{-1}$ , as is known, should be unique.

In fact, as follows from the above, the Hohenberg–Kohn lemma is insufficient for the statement about the existence of the universal solution  $v(\mathbf{r}, [n])$ . However, it seems impossible to disprove the statement about the universality in the general form. We therefore use the proof by contradiction. We assume that the functional  $v(\mathbf{r}) = v(\mathbf{r}, [n])$  exists and analyze consequences of this statement. With the example of noninteracting fermions, we show that such an assumption leads to a contradiction.

If we accept the validity of statement (1), then the ground-state energy  $E_0$  of the system of  $N$  interacting electrons with a Hamiltonian  $H$  in the external field with the potential  $v(\mathbf{r})$ , which is characterized by the wave function  $\Psi_0$ , can be written as

$$E_0 \equiv \langle \Psi_0 | H | \Psi_0 \rangle = E_0(N, [\Psi_0], [v]) = E_0([n], [v]), \quad N = \int n(\mathbf{r}) d^3\mathbf{r}. \quad (2)$$

Here, it is taken into account that  $\langle \Psi_0 | \Psi_0 \rangle = 1$  and  $\Psi_0 = \Psi_0[v] = \Psi_0[v + \text{const}]$ . In turn, it immediately follows from (2) that the quantity  $F[n] = \langle \Psi_0 | T + U | \Psi_0 \rangle$ , which defines the system ground-state energy

$$E_0([n], [v]) = F[n] + \int v(\mathbf{r})n(\mathbf{r}) d^3\mathbf{r}, \quad (3)$$

is a functional of only the density  $n(\mathbf{r})$  ("universal" density functional). In this case, it is admissible to use the term "universal" in the sense of the independence of its explicit form of the external field potential [1, 2], although this requires considering the  $v$ -representability and  $N$ -representability of the inhomogeneous density.

The operators  $T$  and  $U$  are respectively the kinetic and interparticle interaction energy operators. Statement (3) is the basis of the DFT widely used in various areas of physics and chemistry (see, e.g., [4, 5]). However, the exact form of this universal functional is still unknown even for noninteracting electrons ( $U = 0, N > 1$ ). It is clear that there is a one-to-one correspondence between the statements about the existence of the functionals  $v(\mathbf{r}, [n])$  and  $F[n]$ , i.e., the existence of one of these functionals predetermines the existence of the other. Hence, if the functional  $F[n]$  in (3) does not exist, the functional  $v(\mathbf{r}, [n])$  also does not exist [3].

### 3. THE DENSITY FUNCTIONAL PROBLEM FOR NONINTERACTING ELECTRONS

In view of the foregoing, we consider one nonrelativistic electron of mass  $m$  in a static external field  $v(\mathbf{r})$ . Then the electron steady state characterized by a certain set of quantum numbers  $\alpha$ , including the spin quantum number  $\sigma$ , is completely defined by the wave function  $\Phi_\alpha(\mathbf{r})$  that satisfies the Schrödinger equation

$$\left\{ -\frac{\hbar^2}{2m} \Delta_{\mathbf{r}} + v(\mathbf{r}) \right\} \Phi_\alpha(\mathbf{r}) = \epsilon_\alpha \Phi_\alpha(\mathbf{r}), \quad (4)$$

where  $\epsilon_\alpha$  is the electron energy in the corresponding state. Because the electron energy is independent of spin, each value of  $\epsilon_\alpha$  is doubly degenerate in the spin quantum number, as are other physical quantities, including the inhomogeneous density  $n_\alpha(\mathbf{r})$ . It is customary to solve Eq. (4) for eigenvalues with the boundary condition  $\Phi_\alpha(|\mathbf{r}| \rightarrow \infty) = 0$  (the so-called condition at infinity [6]). With the possibility of considering the

system in a finite volume  $V$ , the boundary condition for Eq. (4) in the most general form is written as

$$\Phi_\alpha(\mathbf{r} \rightarrow \mathbf{S}) = 0, \quad (5)$$

where  $S$  is the surface bounding the volume  $V$ . We further take into account that the wave function  $\Phi_\alpha(\mathbf{r})$  can be considered a real function [6]. Then

$$n_\alpha(\mathbf{r}) = |\Phi_\alpha(\mathbf{r})|^2 = \Phi_\alpha^2(\mathbf{r}), \quad (6)$$

$$\begin{aligned} \nabla_{\mathbf{r}} n_\alpha(\mathbf{r}) &= 2\Phi_\alpha(\mathbf{r}) \nabla_{\mathbf{r}} \Phi_\alpha(\mathbf{r}), \\ \Delta_{\mathbf{r}} n_\alpha(\mathbf{r}) &= 2\Phi_\alpha(\mathbf{r}) \Delta_{\mathbf{r}} \Phi_\alpha(\mathbf{r}) + \\ &+ 2(\nabla_{\mathbf{r}} \Phi_\alpha(\mathbf{r}))(\nabla_{\mathbf{r}} \Phi_\alpha(\mathbf{r})). \end{aligned} \quad (7)$$

It immediately follows from Eqs. (4)–(7) that the inhomogeneous density  $n_\alpha(\mathbf{r})$  satisfies the equation for eigenvalues

$$\begin{aligned} -\frac{\hbar^2}{4m} \Delta_{\mathbf{r}} n_\alpha(\mathbf{r}) + \frac{\hbar^2}{8mn_\alpha(\mathbf{r})} (\nabla_{\mathbf{r}} n_\alpha(\mathbf{r})) \times \\ \times (\nabla_{\mathbf{r}} n_\alpha(\mathbf{r})) + v(\mathbf{r})n_\alpha(\mathbf{r}) = \epsilon_\alpha n_\alpha(\mathbf{r}) \end{aligned} \quad (8)$$

with the boundary conditions

$$n_\alpha(\mathbf{r} \rightarrow \mathbf{S}) = 0, \quad \nabla_{\mathbf{r}} n_\alpha(\mathbf{r})|_{\mathbf{r} \rightarrow \mathbf{S}} = 0. \quad (9)$$

We now integrate Eq. (8) over the volume occupied by the system, using the normalization condition

$$\int n_\alpha(\mathbf{r}) dV = 1 \quad (10)$$

that immediately follows from (6). From (8), we then find the density functional for the energy  $\epsilon_\alpha$ :

$$\epsilon_\alpha([n], [v]) = F^{(1)}[n_\alpha] + \int v(\mathbf{r})n_\alpha(\mathbf{r}) dV, \quad (11)$$

$$F^{(1)}[n_\alpha] = F_0^{(1)}[n_\alpha] + F_W^{(1)}[n_\alpha], \quad (12)$$

$$\begin{aligned} F_0^{(1)}[n_\alpha] &= -\frac{\hbar^2}{4m} \int \Delta_{\mathbf{r}} n_\alpha(\mathbf{r}) dV, \\ F_W^{(1)}[n_\alpha] &= \frac{\hbar^2}{8m} \int \frac{(\nabla_{\mathbf{r}} n_\alpha(\mathbf{r}))(\nabla_{\mathbf{r}} n_\alpha(\mathbf{r}))}{n_\alpha(\mathbf{r})} dV, \end{aligned} \quad (13)$$

where  $F^{(1)}[n_\alpha]$  is the universal density functional  $F[n]$  in Eq. (3) for one particle (superscript (1)). The functional  $F^{(1)}[n_\alpha]$  is written in (12) in the form of two terms for two reasons. First, because of the Gauss formula and the second boundary condition in (9), the functional  $F_0^{(1)}[n_\alpha]$  vanishes,

$$\begin{aligned} F_0^{(1)}[n_\alpha(\mathbf{r})] &= -\frac{\hbar^2}{4m} \int \Delta_{\mathbf{r}} n_\alpha(\mathbf{r}) dV = \\ &= -\frac{\hbar^2}{4m} \oint \nabla_{\mathbf{r}} n_\alpha(\mathbf{r}) d\mathbf{S} = 0. \end{aligned} \quad (14)$$

Second, the functional explicit form  $F_W^{(1)}[n_\alpha]$  in (13) is formally exactly identical to the so-called Weizsäcker correction to the Thomas–Fermi kinetic energy functional [7] (see Refs. [4, 5] for more details). In contrast to the Weizsäcker correction, the expression  $F_W^{(1)}[n_\alpha]$  in (13) in this problem is an exact expression for the “universal” functional of the inhomogeneous density for one particle. Hence, in this case, the “universal” density functional  $F^{(1)}[n_\alpha]$  exists, is found exactly, and is written as

$$F^{(1)}[n_\alpha] = F_W^{(1)}[n_\alpha]. \quad (15)$$

By direct calculation (see, e. g., [5]), it is easy to verify that

$$\begin{aligned} \frac{\delta F_W^{(1)}[n_\alpha]}{\delta n_\alpha(\mathbf{r})} &= -\frac{\hbar^2}{4mn_\alpha(\mathbf{r})}\Delta_{\mathbf{r}}n_\alpha(\mathbf{r}) + \\ &+ \frac{\hbar^2}{8mn_\alpha^2(\mathbf{r})}(\nabla_{\mathbf{r}}n_\alpha(\mathbf{r}))(\nabla_{\mathbf{r}}n_\alpha(\mathbf{r})). \end{aligned} \quad (16)$$

Therefore, Eq. (8) for energy eigenvalues  $\epsilon^{(1)}$  of one particle in the external field  $v(\mathbf{r})$  with boundary conditions (9) is a consequence of the variation equation for the energy  $\epsilon^{(1)}([n^{(1)}, [v]]$  as the inhomogeneous density functional  $n^{(1)}(\mathbf{r})$  of one particle in the specified external field  $v(\mathbf{r})$ ,

$$\delta\epsilon^{(1)}[n^{(1)}] = 0. \quad (17)$$

Indeed, using normalization condition (10) and the Legendre transform, from (17), we find

$$\frac{\delta\epsilon^{(1)}[n^{(1)}]}{\delta n^{(1)}} = \text{const.} \quad (18)$$

To determine the constant in Eq. (18), we take into account that, according to (11)–(16),

$$\frac{\delta F^{(1)}[n^{(1)}]}{\delta n^{(1)}(\mathbf{r})} + v(\mathbf{r}) = \text{const} = \epsilon^{(1)}. \quad (19)$$

Thus, variation equation (17) is equivalent to (8) and is completely identical to the corresponding equation for the wave function functional in quantum mechanics (see, e. g., [6]). Hence, in the one-particle case under consideration, there exists a density functional  $v(\mathbf{r}, [n])$  for the external field potential, determined up to a constant factor,

$$\begin{aligned} v(\mathbf{r}, [n^{(1)}]) + \text{const} &= \frac{\delta F^{(1)}[n^{(1)}]}{\delta n^{(1)}(\mathbf{r})} = \\ &= \frac{\hbar^2}{4mn^{(1)}(\mathbf{r})}\Delta_{\mathbf{r}}n^{(1)}(\mathbf{r}) - \frac{\hbar^2}{8m[n^{(1)}(\mathbf{r})]^2} \times \\ &\times (\nabla_{\mathbf{r}}n^{(1)}(\mathbf{r}))(\nabla_{\mathbf{r}}n^{(1)}(\mathbf{r})). \end{aligned} \quad (20)$$

Therefore, as noted above, the existence of the functional  $F^{(1)}[n^{(1)}]$  in (15) predetermines the existence of the functional  $v(\mathbf{r}, [n^{(1)}])$  in (20), and vice versa.

We note an essential circumstance. According to (20), in the case of one electron, the functional  $v(\mathbf{r}, [n^{(1)}])$  is local:  $v(\mathbf{r}, [n^{(1)}]) = v[n^{(1)}(\mathbf{r})]$ , i. e., the value of the potential  $v(\mathbf{r})$  at a point  $\mathbf{r}$  is determined (up to a constant) by the inhomogeneous density  $n^{(1)}(\mathbf{r})$  at that coordinate. In the general case, if we assume the existence of the density functional, this locality is evidently absent.

Taking into account that the Hohenberg–Kohn lemma proof, as well as statements (1) and (3), are by no means independent of a particular value of the number of particles  $N$  in the system, the assumption on the existence of the “universal” density functional allows extending the results obtained to the case of an arbitrary number of noninteracting electrons.

For this, we consider a system of  $N$  noninteracting electrons in the external field  $v(\mathbf{r})$ . To account for the identity of electrons, it is most convenient to use the secondary quantization formalism (see Refs. [4–6] for more details). We note that this consideration is fully equivalent to the use of Slater determinants to describe the wave function of the system of noninteracting electrons and to implement the Young scheme [5, 6]. Any state of the system of  $N$  noninteracting identical electrons is then characterized by a set of the so-called “occupied” single-particle states  $\alpha_1, \dots, \alpha_N$  (see (4)) and, by virtue of the Pauli principle,

$$\alpha_i \neq \alpha_j \quad \text{for } i \neq j. \quad (21)$$

Then the energy  $E^{(0)}$  and inhomogeneous density  $n^{(0)}(\mathbf{r})$  in a corresponding state are given by [5, 6]

$$\begin{aligned} E^{(0)}(\alpha_1, \dots, \alpha_N) &= \sum_{\alpha_i} \epsilon_{\alpha_i}, \\ n^{(0)}(\mathbf{r}, \alpha_1, \dots, \alpha_N) &= \sum_{\alpha_i} n_{\alpha_i}(\mathbf{r}). \end{aligned} \quad (22)$$

Here,  $\epsilon_{\alpha_i} = \epsilon_{\alpha_i}([n_{\alpha_i}], [v])$  (see (11)–(13)), and  $\sum_{\alpha_i} 1 = N$ . It then immediately follows from (21) and (22) that the energy  $E^{(0)}$  of the system of  $N$  ( $N \geq 3$ ) noninteracting identical electrons, including the ground-state energy  $E_0^{(0)}$ , cannot be the density functional  $n^{(0)}(\mathbf{r})$  in the specified external field due to the nonlinearity of the functional  $F_W^{(1)}[n_{\alpha_i}]$  in (13). It is clear that a similar statement also holds for the universal functional  $\langle \Psi_0 | T | \Psi_0 \rangle$ . This is a consequence of the fact that the external field potential  $v(\mathbf{r})$  for  $N \geq 3$  cannot be presented as the density functional  $n(\mathbf{r})$  (see (20)).

In the case of two noninteracting ground-state electrons, the DFT statements remain valid due to

the double degeneracy in the spin quantum number ( $n(\mathbf{r}) = 2n^{(1)}(\mathbf{r})$ ; see, e. g., [8]). We also note that these results are directly associated with the Pauli principle, which applies only to fermions. In the case of ground-state bosons, which are “accumulated” at one lowest energy level (Bose condensation), the DFT statements remain valid at an arbitrary number of noninteracting bosons.

Thus, for more than two noninteracting fermions in the inhomogeneous ground state, the external field potential  $v(\mathbf{r})$  is not the density functional  $n(\mathbf{r})$ , i. e.,  $v(\mathbf{r}) \neq v(\mathbf{r}, [n])$ .

#### 4. THE DENSITY FUNCTIONAL PROBLEM FOR INTERACTING ELECTRONS

We now show that the obtained results lead straightforwardly to the validity of an analogous conclusion for the system of interacting electrons. The Hamiltonian of the system of inhomogeneous electrons can be written as

$$H_\lambda = T + \int d\mathbf{r} v(\mathbf{r})\hat{n}(\mathbf{r}) + \lambda U, \quad (23)$$

where  $\hat{n}(\mathbf{r})$  is the electron density operator,  $\langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_0 \rangle = n(\mathbf{r})$ , and  $U$  is the operator of the electron interaction energy. Then the energy  $E_0(\lambda)$  of the ground state  $\Psi_0(\lambda)$  satisfies the equality (see, e. g., [9])

$$\frac{\partial E_0(\lambda)}{\partial \lambda} = \langle \Psi_0(\lambda) | \frac{\partial H_\lambda}{\partial \lambda} | \Psi_0(\lambda) \rangle = \langle \Psi_0(\lambda) | U | \Psi_0(\lambda) \rangle. \quad (24)$$

This straightforwardly implies an explicit relation for the ground-state energy of the system of interacting electrons:

$$E_0 - E_0^{(0)} = \int_0^1 \frac{d\lambda}{\lambda} \langle U \rangle_\lambda, \quad (25)$$

where  $E_0^{(0)}$  is the ground-state energy of the inhomogeneous electron gas without interaction, which has been calculated above, and  $\langle U \rangle_\lambda$  is the average potential energy of the inhomogeneous electron system with Hamiltonian (23). We next recall that if the density functional  $v(\mathbf{r}, [n])$  exists, the average kinetic energy, as well as average potential energy, of the inhomogeneous electron system is the universal density functional [10]. It is obvious that presence of the parameter  $\lambda$  in Hamiltonian (23) has no effect on this statement as well as the integration in Eq. (25). It then directly follows

from (25) that for the existence of the universal density functional  $F[n]$  (see (3)) requires the existence of the universal density functional for the inhomogeneous electron system without interaction. This is impossible, as was shown above, for more than two Fermi particles.

In a different way, the impossibility of the existence of the density functional of an inhomogeneous electron system follows from the fact that the terms in the perturbation theory series for energy, which contain the interaction potential, have a different nature than the terms without interaction. Therefore, they cannot compensate the “non-universality” of the kinetic energy of noninteracting electrons.

#### 5. THE DENSITY MATRIX FUNCTIONAL THEORY

As a result, we come to the conclusion that the Hohenberg–Kohn lemma [1, 2] cannot be a justification of the existence of a “universal” density functional as a precise statement or a theorem. At the same time, in various approximations (e. g., in the limit of weak inhomogeneity of the external field or in the semiclassical limit for the electron gas), the “universal” functional can exist. In this relation, we note the following. The leading approximation for density functional construction is the so-called local density approximation (LDA) (see [4, 5, 10] for the details). The basis of LDA is the dependence of the energy of a homogeneous electron gas on the average density  $n$ , which is equal to the ratio of the total number  $N$  of electrons to the volume  $V$ ,  $n = N/V$ . The analysis of an homogeneous electron gas is in turn based on use of the thermodynamic limit transition  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $N/V \rightarrow n \neq 0$  (see, e. g., [9]). This means that the model of a homogeneous electron system cannot be used as the initial approach for considering a finite number of electrons in an external field (in particular, in the case of electrons in the field of one or several nuclei, when the conditions of the thermodynamic limit transition are not valid even for a nuclear charge  $Z \gg 1$ ).

In this relation, we note that the Hohenberg–Kohn lemma is correct not only for an inhomogeneous density  $n(\mathbf{r})$  but also for the single-particle density matrix

$$\rho^{(1)}(\mathbf{r}, \mathbf{r}') = \langle \Psi_0 | \Psi^\dagger(\mathbf{r}) \Psi(\mathbf{r}') | \Psi_0 \rangle \quad (26)$$

(see [11, 12] for the details). This is easy to verify taking into account that the inhomogeneous density  $n(\mathbf{r}) = \rho^{(1)}(\mathbf{r}, \mathbf{r})$  is completely determined if the density matrix is known (the opposite statement is, in general, incorrect). Then, instead statement (1) which, as

shown above, is the basis of the DFT, we can use a similar statement for the single-particle density matrix  $\rho^{(1)}(\mathbf{r}, \mathbf{r}')$ ,

$$\begin{aligned} \rho^{(1)}(\mathbf{r}, \mathbf{r}') &= \rho^{(1)}(\mathbf{r}, \mathbf{r}'; [v]) \rightarrow v(\mathbf{r}) + \text{const} = \\ &= v(\mathbf{r}; [\rho^{(1)}]). \end{aligned} \quad (27)$$

## 6. CONCLUSIONS

The approach in this paper is the basis of the theory of the density matrix functional (TDMF), originated from Hilbert's theorem [13] (the abbreviation TDMF must be distinguished from DMFT for the dynamic mean field theory). In the TDMF framework, the value  $F$  in (3) becomes the universal density matrix functional:  $F = F[\rho^{(1)}]$  [14]. However, as in case (1), it is impossible to prove statement (27) in the general case. Nevertheless, the TDMF has a wide application for the study of the inhomogeneous electron gas properties (see, e.g., [15, 16] and the references therein). This is because the TDMF, in contrast to the DFT [17], provides the correct description of the inhomogeneous electron gas in both the ideal gas approach and the self-consistent Hartree–Fock approximation [14–16]. The situation under consideration is similar to the one for classical liquids, where numerous closed equations for the pair correlation function can be formulated with various choices for the generating functionals (see, e.g., [18]). Such a choice is limited only by the conditions of a consistent theory and agreement with experimental data. The fulfillment of the second requirement in the case of an inhomogeneous electron gas is restricted because there is no direct way to experimentally measure the inhomogeneous density  $n(\mathbf{r})$  (and the single-particle density matrix  $\rho^{(1)}(\mathbf{r}, \mathbf{r}')$ ) as a function of the coordinate. We can be guided only by the energetic characteristics of the systems of interacting particles, which are integral values based on local functions  $n(\mathbf{r})$  and  $\rho^{(1)}(\mathbf{r}, \mathbf{r}')$ . Therefore, the condition of a self-consistent theoretical foundation plays a primary role. The above consideration shows that the TDMF approach is preferable in this sense.

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