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From the density functional theory to the single-particle green function

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Abstract: An analysis shows that the ground state of inhomogeneous system of interacting electrons in the static external field, which satisfies the thermodynamic limit, can be consistently described only using the Green function theory based on the quantum field theory methods (diagram technique of the perturbation theory). In this case, the ground state energy and the inhomogeneous electron density in such a system can be determined only after calculating the single-particle Green function.

Keywords: Density functional theory; Virial theorem; Green functions

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1. Introduction

Although more than 50 years is elapsed from the time of the publication of the known paper by Hohenberg–Kohn [1], the principal problem of the density functional theory (DFT) on the procedure for calculating the universal density functional has not yet been solved [2–4]. Moreover, in the study of the electronic structure of matter, the reduced density matrix functional theory (RDMFT) [5–8], dynamical mean-field theory (DMFT) [9, 10], which are the approximal schemes in the framework of the Green function theory (GFT) for the many-body system [11–14], have gained wide acceptance in recent years. In this situation, the problem of the relation between these theories arises quite naturally [15–17]. To solve this problem in the present paper the critical analysis of the main provisions of the DFT is performed. This analysis shows that the consequent description of the ground state of inhomogeneous interacting electron system in a static external field is possible only by using the Green functions theory. The Green function theory, as is known, is based on the quantum field theory methods (diagram technique of the perturbation theory) and implies the consideration within the quantum statistical theory.

2. Density functional for the external field potential

According to the Hohenberg–Kohn lemma which is often referred to as the first Hohenberg–Kohn theorem, 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 non-relativistic electronic system (except for the case $v_1(\mathbf{r}) - v_2(\mathbf{r}) = \text{const}$) [1]. This statement is mathematically rigorous and is beyond question. Thus, the inhomogeneous density $n(\mathbf{r})$ of the non-relativistic ground-state electronic system uniquely corresponds to the external field potential $v(\mathbf{r})$ (to within an additive constant). In other words, the inhomogeneous density $n(\mathbf{r})$ in the ground state is the unique functional of the external field $v(\mathbf{r})$ (to within an additive constant),

$$n(\mathbf{r}) \equiv \langle \Psi^+(\mathbf{r})\Psi(\mathbf{r})\rangle_0 = n(\mathbf{r}, [v]). \tag{1}$$

Here $\Psi^+(\mathbf{r})$ and $\Psi(\mathbf{r})$ are, respectively, the field operators of creation and annihilation for electrons (hereafter, we omit spin indices), the angle brackets with zero index mean averaging over the ground state of the electronic system in the static external field.

The next stage of the DFT construction consists of the statement that, according to Eq. (1), the external field potential is the inhomogeneous ground-state density functional [1, 18],

$$v(\mathbf{r}) = v(\mathbf{r}, [n]) + \text{const.} \tag{2}$$

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From statement (2), the Hohenberg–Kohn theorem (or the second Hohenberg–Kohn theorem) [1] immediately follows, which states that in the ground state energy

$$E_0 = \langle \hat{K} + \hat{U} \rangle_0 + \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \qquad (3)$$

the universal density functional

$$F[n] = \langle \hat{K} + \hat{U} \rangle_0, \qquad (4)$$

can be separated. Here $\hat{K}$ and $\hat{U}$ are the kinetic energy and electron interparticle interaction energy operators, respectively. The term "universal" means that the corresponding functional does not explicitly depend on the external field potential $v(\mathbf{r})$. However, in this case, it should be taken into account that the inhomogeneous density of the ground state is a $v(\mathbf{r})$-representable function, i.e., the function $n(\mathbf{r})$ corresponds to the external field potential $v(\mathbf{r})$, which immediately follows from the proof of the Hohenberg–Kohn lemma. Furthermore, the inhomogeneous density should be a N-representable function

$$N = \int n(\mathbf{r}) d\mathbf{r}. \qquad (5)$$

Thus, if statement (2) is valid, the ground state energy E_0 becomes a functional of the inhomogeneous density $n(\mathbf{r})$ and the external field potential $v(\mathbf{r})$

$$E_0([n], [v]) = F[n] + \int v(\mathbf{r}) \, n(\mathbf{r}) d\mathbf{r}. \qquad (6)$$

Equation (6) is a basis for practical application of the DFT [1–4, 18]. In fact, for the transition from the initial functional $E_0[v]$ to the functional $E_0([n], [v])$ in Eq. (6) the Legendre transformation for the value $F[n]$ is implied. Initially, the value F is the functional $F[v]$. In this case, the derivation of the variational equation for determining the inhomogeneous density $n(\mathbf{r})$ of the ground state is based on the known inequality which is used to prove the Hohenberg–Kohn lemma [1]

$$E_0^{(1)} \le E_0^{(2)} + \langle \Psi_0^{(2)} | \hat{H}_1 - \hat{H}_2 | \Psi_0^{(2)} \rangle. \qquad (7)$$

Here $E_0^{(i)} = \langle \Psi_0^{(i)} | \hat{H}_i | \Psi_0^{(i)} \rangle$ is the ground state energy of the system with the Hamiltonian $\hat{H}_i$ which corresponds to the wave function $\Psi_0^{(i)}$. From the inequality (7), taking into account Eq. (6), it immediately follows that

$$\varepsilon([n], v) \le \varepsilon([\tilde{n}], v), \qquad (8)$$

where the value $\varepsilon([\tilde{n}], v)$ according the definition equals

$$\varepsilon([\tilde{n}], v) = F(\tilde{n}) + \int v(\mathbf{r}) \tilde{n}(\mathbf{r}) d\mathbf{r}. \qquad (9)$$

Here $\tilde{n}(\mathbf{r}) = \tilde{n}(\mathbf{r}, [\tilde{v}])$ is the inhomogeneous density of the ground state, corresponding to the external field $\tilde{v}(\mathbf{r})$ and

normalization condition $\int \tilde{n}(\mathbf{r}) d\mathbf{r} = N$. In other words, the inhomogeneous density $\tilde{n}(\mathbf{r})$ is a v-representable and N-representable function. Note, that the value $\varepsilon([\tilde{n}], v)$ is an auxiliary function. Taking also Eqs. (6)–(9) into account, it is easy to check that the quantity ε only under the condition $\tilde{n}(\mathbf{r}) = n(\mathbf{r})$ is identical to the ground state energy E_0 in the given external field $v(\mathbf{r})$: $\varepsilon([n], v) = E_0$. Inequality (8) can be presented as a variational equation for determining the unknown function $\tilde{n}(\mathbf{r})$

$$\delta \varepsilon([\tilde{n}], v) = 0 \qquad (10)$$

in the given external field $v(\mathbf{r})$ at the given number of particles $N = \int \tilde{n}(\mathbf{r}) d\mathbf{r}$. Till now, the obtaining of the general solution for Eq. (10) does not seem possible. Thus, in the framework of the DFT to find the solution of this equation the Lagrange multiplier method is used. Within this method, the basic DFT equation for calculating the inhomogeneous density $\tilde{n}(\mathbf{r})$

$$\frac{\delta F[\tilde{n}]}{\delta \tilde{n}(\mathbf{r})} + v(\mathbf{r}) = \lambda \qquad (11)$$

follows from the variation equation $\delta \{ \varepsilon([\tilde{n}], v) - \lambda (\int \tilde{n}(\mathbf{r}) d\mathbf{r} - N) \} = 0$ which is equivalent to Eq. (10) taking into account the condition $\int \tilde{n}(\mathbf{r}) d\mathbf{r} = N = const$ and the definition (9). Here λ is the Lagrange multiplier which is independent of the variable $\mathbf{r}$. The solution of Eq. (11) for the inhomogeneous density $\tilde{n}(\mathbf{r})$, corresponding to the external field $\tilde{v}(\mathbf{r})$, is identical to the inhomogeneous density of the ground state $n(\mathbf{r})$, corresponding to the given external field $v(\mathbf{r})$. Thus, when using hypothesis (2) about the functional $v(\mathbf{r}; [n])$, the problem is reduced to the determination of the universal density functional $F([\tilde{n}])$ [Eq. (4)] and its variational derivative. However, as noted above, a consistent procedure for determining this universal functional has not yet been developed. To resolve this situation, we will proceed from the fact that the variational Eq. (11) is a direct consequence of the hypothesis (2) about the existence of the functional for the external field potential $v(\mathbf{r}; [n])$ [18]. According to Eq. (9), the universal functional variation δF which is related to the inhomogeneous density variation $\delta \tilde{n}(\mathbf{r})$, is caused by the variation of the total number of particles $\delta N = \int \delta \tilde{n}(\mathbf{r}) d\mathbf{r}$ and the variation of the external field potential $\delta \tilde{v}(\mathbf{r})$. This statement is a consequence of the fact that the inhomogeneous density $\tilde{n}(\mathbf{r})$ should be an N-representable and v-representable function. In other words, the variational principle Eq. (10) cannot to be used in practical calculations, if the trial function is not an N-representable and v-representable function [2]. According to the problem condition, the total number of particles N in the system is given ($N = const$) and is independent of the

external field potential. Therefore, the variational Eq. (10) should be written as

$$\delta\varepsilon([\tilde{n}], v) = 0; \quad \delta N = \int \delta\tilde{n}(\mathbf{r})d\mathbf{r} = 0. \tag{12}$$

In this case

$$\frac{\delta F[\tilde{n}]}{\delta\tilde{n}(\mathbf{r})} = \int \frac{\delta F(N, [\tilde{v}(\mathbf{r}); [\tilde{n}]])}{\delta\tilde{v}(\mathbf{r}_1)} \frac{\delta\tilde{v}(\mathbf{r}_1)}{\delta\tilde{n}(\mathbf{r})}d\mathbf{r}_1 \tag{13}$$

and Eq. (11) takes the form

$$\int \frac{\delta F(N, [\tilde{v}(\mathbf{r}; [\tilde{n}])])}{\delta\tilde{v}(\mathbf{r}_1)} \frac{\delta\tilde{v}(\mathbf{r}_1)}{\delta\tilde{n}(\mathbf{r})}d\mathbf{r}_{1\,|N=const} + v(\mathbf{r}) = \lambda. \tag{14}$$

Taking into account the determination Eq. (9) one can find

$$\frac{\delta F(N, [\tilde{v}(\mathbf{r}; [\tilde{n}])])}{\delta\tilde{v}(\mathbf{r})} = \frac{\delta\tilde{E}_0(N, [\tilde{v}(\mathbf{r}; [\tilde{n}])])}{\delta\tilde{v}(\mathbf{r})} - \tilde{n}(\mathbf{r})$$
$$- \int \tilde{v}(\mathbf{r}_1)\frac{\delta\tilde{n}(\mathbf{r}_1)}{\delta\tilde{v}(\mathbf{r})}d\mathbf{r}_1, \tag{15}$$

where $\tilde{E}_0$ is the energy of the ground state in an external field $\tilde{v}(\mathbf{r})$, which corresponds to the inhomogeneous density $\tilde{n}(\mathbf{r})$. For simplicity, here and below the index $N = const$ is omitted. Substituting Eq. (15) into Eq. (14) and taking into account the explicit equalities

$$\frac{\delta\tilde{E}_0(N, [\tilde{v}(\mathbf{r}; [\tilde{n}])])}{\delta\tilde{v}(\mathbf{r})} = \tilde{n}(\mathbf{r}), \quad \int \frac{\delta\tilde{v}(\mathbf{r}')}{\delta\tilde{n}(\mathbf{r}_1)}\frac{\delta\tilde{n}(\mathbf{r}_1)}{\delta\tilde{v}(\mathbf{r})}d\mathbf{r}_1 = \delta(\mathbf{r} - \mathbf{r}') \tag{16}$$

one can obtain the exact equation for determination of the inhomogeneous density in the framework of DFT

$$v(\mathbf{r}) = \tilde{v}(\mathbf{r}; [\tilde{n}]) + \lambda, \tag{17}$$

where λ is exactly the constant to within which the Hohenberg–Kohn lemma is valid. Thus, if the hypothesis (2) about the functional $v(\mathbf{r}; [n])$ existence is valid, the solution of the DFT problem on the inhomogeneous density calculation in a given external field is reduced to the determination of such an inhomogeneous density $\tilde{n}(\mathbf{r})$ which corresponds to the external field $\tilde{v}$ and leads to the given external field potential $v(\mathbf{r})$. In the course of the above derivation of Eq. (17), an explicit form of the universal density functional is not used, and the possibility of calculating the variational derivative $\frac{\delta F[\tilde{n}]}{\delta\tilde{n}(\mathbf{r})}$ is caused only by the requirement that the inhomogeneous density $\tilde{n}(\mathbf{r})$ should be an N-representable and v-representable function. As a result, if the hypothesis about the existence of the functional $v(\mathbf{r}; [n])$ is valid, the basic DFT problem is the determination of the explicit form of this functional.

However, this problem can be solved only when considering one electron in the static external field [19], since the inhomogeneous density $n(\mathbf{r})$ in this case has the form

$$n(\mathbf{r}) = |\varphi_0(\mathbf{r})|^2 = \varphi_0^2(\mathbf{r}), \tag{18}$$

where $\varphi_0(\mathbf{r})$ is the wave function of the ground-state electron energy $\tilde{E}_0$ in the static external field, which satisfies the Schrödinger equation

$$(\hat{K} + \hat{U})\varphi_0(\mathbf{r}) = \varepsilon_0\varphi_0(\mathbf{r}), \tag{19}$$

and, without loss of generality, is a real function. In this case, it is clear that Eq. (2) takes the form

$$v(\mathbf{r}) = v[n(\mathbf{r})] + \text{const}. \tag{20}$$

When considering more than two noninteracting electrons, as shown in Ref. [19], the functional $v(\mathbf{r}, [n])$ cannot be constructed. The existence of the universal density functional for two noninteracting electrons is caused by electron energy degeneracy with respect to the spin quantum number in the non-relativistic consideration. In the general case, the initial functional $n(\mathbf{r}, [v])$ is nonlinear in the external field $v(\mathbf{r})$. This means that, without violation of the Hohenberg–Kohn lemma, the two possibilities are allowed:

1. the inverse problem on the determination of 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 function pairs $n(\mathbf{r})$ and $v(\mathbf{r})$);
2. the inverse problem has the universal solution $v(\mathbf{r}) = v(\mathbf{r}, [n])$.

Usually, this dilemma is not considered; however, it is assumed that the universal solution $v(\mathbf{r}, [n])$ takes place, which is valid for any external field and any number of particles [20]. The similar problems have been also discussed elsewhere [21, 22]. The essence of the problem at hand can be expressed in other words. We introduce in the consideration the operator $\hat{P}$ relating the functions $n(\mathbf{r})$ and $v(\mathbf{r})$: $n(\mathbf{r}) = \hat{P}v(\mathbf{r})$. In this case, the operator $\hat{P}$ is such that the equality $\hat{P}v(\mathbf{r}) = \hat{P}\{v(\mathbf{r}) + \text{const}\}$ is valid. It follows from Eq. (1) for the inhomogeneous density $n(\mathbf{r})$ that the operator $\hat{P}$ is nonlinear. Thus, the problem of determining the inverse operator $\hat{P}^{-1}$ relating the functions $v(\mathbf{r})$ and $n(\mathbf{r})$ as $v(\mathbf{r}) = \hat{P}^{-1}n(\mathbf{r})$ has not a unique solution in the general case. As a result, statement (2) about the existence of the density functional for the external field potential is not valid when considering the multielectron system. Therefore, the proof of the existence of the universal density functional $F[n]$ [Eq.(4)] is absent although the Hohenberg–Kohn lemma about the functional $n(\mathbf{r}, [v])$ uniqueness [19, 20] is valid.

3. Results and discussion

3.1. Virial theorem and the reduced density matrix

We would like to retain the main idea in describing the multielectron system, i.e., to use functions of a small

number of spatial variables, rather than many-particle wave functions. We take into account that the inhomogeneous density $n(\mathbf{r})$ is a diagonal element of the reduced density matrix

$$\gamma(\mathbf{r}, \mathbf{r}') = \langle \Psi^+(\mathbf{r})\Psi(\mathbf{r}')\rangle_0 = \gamma(\mathbf{r}, \mathbf{r}'; [v]), \quad n(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r}). \tag{21}$$

Thus, the statement similar to the Hohenberg–Kohn lemma for the inhomogeneous density $n(\mathbf{r})$ is valid for the function $\gamma(\mathbf{r}, \mathbf{r}')$, i.e., the functional $\gamma(\mathbf{r}, \mathbf{r}'; [v])$ is unique. Therefore, instead of statement (2), we can assume that the external field potential is the functional of the reduced density matrix,

$$v(\mathbf{r}) = v(\mathbf{r}, [\gamma]) + \text{const}. \tag{22}$$

In this case, instead of the universal density functional $F[n]$ [Eq. (4)], we obtain the universal functional of the reduced density matrix,

$$\Phi[\gamma] = \langle \hat{K} + \hat{U}\rangle_0. \tag{23}$$

The statement (23) is a basis of the RDMFT which, in contrast to the DFT, is valid for both the arbitrary number of noninteracting electrons and for the self-consistent Hartree-Fock approximation [5–7]. We should mention that Eq. (23) is directly related to the Hilbert theorem [23] which establishes the single-valued correspondence between the reduced density matrix in an inhomogeneous system and the nonlocal external field static potential.

Let us also pay attention that the DFT results do not follow from the RDMFT, although the assumption that the reduced density matrix is the inhomogeneous density functional $\gamma(\mathbf{r}, \mathbf{r}') = \gamma(\mathbf{r}, \mathbf{r}'; [n])$ is often used [5–7]. In addition to the absence of the corresponding proof, the results of the self-consistent Hartree-Fock approximation cannot be used within the DFT [24]. However, the possible existence of the universal functional of the reduced density matrix is based on Eq. (22) which, as in the case of Eq. (3) for the DFT, cannot be proved. As a result, we face with the absence of a regular procedure for determining the universal functional $\Phi[\gamma]$ [Eq. (23)] when considering the inhomogeneous system of interacting electrons. In this context, we note that if we take the existence of the universal density functional $F[n]$ [Eq. (4)] as a postulate, the existence of the functional $v(\mathbf{r}, [n])$ will be a strict result of the DFT [25]. In fact, this means that the existence of the density functional for the external field potential given by Eq. (2) follows from the existence of the universal density functional (4). It is clear that a similar statement is valid within the RDMFT as well, i.e., Eq. (23) follows from Eq. (22). Thus, the used method for proving the existence of the universal reduced density functional $\Phi[\gamma]$ is strictly speaking incorrect. In this situation, we cannot consider the

statement (10) as a postulate, at least, until proved otherwise, e.g., with respect to the universal functional $F[n]$.

Therefore, we can formulate the problem as follows. Let the reduced density matrix $\gamma(\mathbf{r}, \mathbf{r}')$ is known a priori. We should indicate a method for calculating the ground state energy E_0 for the system of interacting electrons in the static external field $v(\mathbf{r})$ by the known reduced density matrix $\gamma(\mathbf{r}, \mathbf{r}')$. In solving the posed problem, we should take into account the fact that the system under consideration is in the volume V which is as a rule defined by the volume of a "box" with infinite potential walls (closed system). Therefore, the wave function Ψ_0 of such a system vanishes once at least one spatial variable of the wave function appears on the surface S bounding the volume V, $\Psi_0|_S = 0$. This condition is equivalent to the boundary condition "at infinity" for wave functions in quantum mechanics, where $V \to \infty$ [26]. Thereby, at first sight, taking into account the boundary condition for wave functions, the passage to the limit $V \to \infty$ makes it possible to "get rid" of the parameter V. However, the result of the passage to the limit $V \to \infty$ depends strongly on the relation between the total number of particles N and the volume V occupied by the system [27, 28]. In this regard, two cases are possible when considering the limit $V \to \infty$:

1. the quantum-mechanical consideration of the finite number of electrons N in the static external field providing finite motion of electrons. Such a consideration is typical for describing electrons in atoms, molecules and corresponds to the condition for the inhomogeneous density, which can be written as

$$\lim_{v \to 0} n(\mathbf{r}) = 0. \tag{24}$$

2. the quantum-statistical consideration where the transition to the thermodynamic limit $V \to \infty, N \to \infty$, $N/V = \bar{n} = const \neq 0$ is performed. Here $\bar{n}$ is the average density of the number of particles (electrons in the case at hand) in the system. Such a consideration is typical for describing electrons in condensed media. In this case, the condition

$$\lim_{v \to 0} n(\mathbf{r}) = \bar{n} \tag{25}$$

is valid, which means that the inhomogeneous density $n(\mathbf{r})$ is identical to the average density $\bar{n}$ of the number of particles in the absence of external field $v(\mathbf{r})$.

Thus, the difference between the considered cases is associated with the notion of the average density $\bar{n}$ of the number of particles, which is obviously independent of the external field potential $v(\mathbf{r})$. When considering the case (1), the system of interacting electrons is in an external field $v(\mathbf{r})$ providing finite motion in a finite space region. Using the virial theorem, it can be shown [29] that

$$E_0 = \langle \hat{K} \rangle_0 - \int \{2n(\mathbf{r}) + \mathbf{r} \cdot \nabla_{\mathbf{r}} n(\mathbf{r})\} v(\mathbf{r}) d\mathbf{r}. \qquad (26)$$

Other words, according to Eqs. (21) and (26) the energy of ground state of the considering system in an external field $v(\mathbf{r})$ can be found by use the known reduced density matrix $\gamma(\mathbf{r}, \mathbf{r}')$ since the average kinetic energy equals

$$\langle \hat{K} \rangle_0 = -\frac{\hbar^2}{2m} \int \{\nabla_{\mathbf{r}'}^2 \gamma(\mathbf{r}, \mathbf{r}')\} \delta(\mathbf{r} - \mathbf{r}') d\mathbf{r} d\mathbf{r}', \qquad (27)$$

where m is the electron mass. However, in the case (2), it is insufficient to know the reduced density matrix $\gamma(\mathbf{r}, \mathbf{r}')$ for determining the ground state energy of the inhomogeneous system of interacting electrons, corresponding to the thermodynamic limit. An exception is the system of noninteracting electrons [Eq. (27)], and the use of the self-consistent Hartree-Fock approximation. Thus, when considering the inhomogeneous system of interacting electrons, corresponding to the thermodynamic limit, in the general case, there is no reason for statements given in Eqs. (22) and (23).

3.2. Single particle Green function and Fermi-liquid theory

To get rid of the need to use the statements for the external field potential, similar to Eqs. (2) and (22), it is necessary to specify such a function for describing the inhomogeneous electronic system in the static external field, which uniquely defines the ground state energy of the system under consideration.

The solution of this problem is possible based on the Gibbs grand canonical distribution with specified chemical potential μ, introducing the time single-particle Green function

$$g(\mathbf{r}, t; \mathbf{r}', t') = -i \langle \hat{T} \{\tilde{\Psi}(\mathbf{r}, t) \tilde{\Psi}^+(\mathbf{r}', t')\} \rangle_0, \qquad (28)$$

where $\tilde{\Psi}^+(\mathbf{r}', t')$ and $\tilde{\Psi}(\mathbf{r}, t)$ are the field operators of creation and annihilation, respectively, for electrons in the Heisenberg representation with exact system Hamiltonian, and $\hat{T}$ is the temporal ordering operator [30]. Hereafter, Planck's constant is $\hbar = 1$. We should underline that the present analysis is performed for the non-relativistic electrons in an external scalar field. This also means the consideration is performed in Euclidian space. The description of the relativistic electron system goes out of the frame of this paper. From Eq. (28), it immediately follows that

$$\gamma(\mathbf{r}, \mathbf{r}') = -i \lim_{t' \to t+0} g(\mathbf{r}, t; \mathbf{r}', t'). \qquad (29)$$

Hence, for the Green function $g(\mathbf{r}, t; \mathbf{r}', t')$, the statement similar to the Hohenberg–Kohn lemma for the

inhomogeneous density $n(\mathbf{r})$ is valid, i.e., the functional $g(\mathbf{r}, t; \mathbf{r}', t'; [v])$ is unique. In other words, the Green function $g(\mathbf{r}, t; \mathbf{r}', t')$ is the v-representative function for the non-relativistic electron system. In this case, this function is calculated using the well developed methods of the quantum field theory (diagram technique for the the the perturbation theory) [30]. In particular, for the Green function $g(\mathbf{r}, \mathbf{r}'; \omega)$ which is the Fourier transform of the function $g(\mathbf{r}, t; \mathbf{r}', t')$ with respect to the variable $(t - t')$, the inhomogeneous Dyson equation

$$g^{-1}(\mathbf{r}, \mathbf{r}'; \omega) = g_0^{-1}(\mathbf{r}, \mathbf{r}'; \omega) - \Sigma(\mathbf{r}, \mathbf{r}'; \omega) \qquad (30)$$

is valid, where the electron self-energy $\Sigma(\mathbf{r}, \mathbf{r}'; \omega)$ is the functional of the exact Green function $g(\mathbf{r}, \mathbf{r}'; \omega)$. The last one is an infinite functional series in powers of the electron-electron interaction potential and single-particle Green functions,

$$\Sigma(\mathbf{r}, \mathbf{r}'; \omega) = \Sigma(\mathbf{r}, \mathbf{r}'; \omega; [g]), \qquad (31)$$

$g_0(\mathbf{r}, \mathbf{r}'; \omega)$ is the Green function for the system of noninteracting ground-state electrons [30],

$$g_0(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{\varepsilon_{0,k} > \mu} \frac{\varphi_{0k}^*(\mathbf{r}') \varphi_{0k}(\mathbf{r})}{\omega - \varepsilon_{0k} + i0} + \sum_{\varepsilon_{0,k} < \mu} \frac{\varphi_{0k}^*(\mathbf{r}') \varphi_{0k}(\mathbf{r})}{\omega - \varepsilon_{0k} - i0}. \qquad (32)$$

Here $\varphi_{0k}(\mathbf{r})$ and ε_{0k} are the electron wave function and the energy, respectively, which are defined by the single-particle Schrödinger equation (see Eq. (19)). In this case, Eq. (29) takes the form

$$\gamma(\mathbf{r}, \mathbf{r}') = -i \lim_{t \to +0} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} g(\mathbf{r}, \mathbf{r}'; \omega) \exp(i\omega t). \qquad (33)$$

In this case, the chemical potential μ can be found for a given average density (taking into account the electron spin),

$$\bar{n} = \bar{n}(\mu) = -\frac{i}{V} \lim_{t \to +0} \int d^3 r \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} g(\mathbf{r}, \mathbf{r}; \omega) \exp(i\omega t). \qquad (34)$$

On this basis, it can be shown that the quantity $\langle \hat{K} + \hat{U} \rangle_0$ is the universal functional $G([g])$ of the single-particle Green function $g(\mathbf{r}, \mathbf{r}'; \omega)$ [9, 31],

$$G[g] = \langle \hat{K} + \hat{U} \rangle_0 = -i \lim_{t \to +0} \int d^3 r d^3 r'$$
$$\times \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \exp(i\omega t) \left\{ \left[-\frac{1}{2m} \nabla_{\mathbf{r}'}^2 g(\mathbf{r}, \mathbf{r}', \omega) \right] \right.$$
$$\left. \delta(\mathbf{r} - \mathbf{r}') + \frac{1}{2} \Sigma(\mathbf{r}, \mathbf{r}', \omega; [g]) g(\mathbf{r}, \mathbf{r}', \omega) \right\}. \qquad (35)$$

Using Eq. (35), we can construct the Luttinger-Ward [32] and the Kadanoff-Baym [33] dynamic variation procedure

for determining the single-particle Green function [34]. Thus, using the GFT based on the quantum field theory methods, we obtain the consistent description of the ground state of the inhomogeneous electronic system in the static external field, which satisfies the thermodynamic limit, without the consideration of the problem of the functional for the external field potential (see Eqs. (2) and (22)).

In this case, an important remark should be made. As follows from Eq. (35), the functional $G([g])$ essentially depends on the functional $\Sigma(\mathbf{r}, \mathbf{r}'; \omega; [g])$. At the same time, according to Eq. (30), this functional directly defines the single-particle Green function, i.e., Eq. (30) is a functional equation for calculating the Green functions $g(\mathbf{r}, \mathbf{r}'; \omega)$. Wherein, the functional $\Sigma(\mathbf{r}, \mathbf{r}'; \omega; [g])$ is nonlinear. This makes the Dyson equation (30) non-linear, so it may also lead to unphysical solutions (see Ref. [35] for a recent discussion). If we have the solution to Eq. (30), inhomogeneous density $n(\mathbf{r})$ is determined from Eqs. (21) and (33). It is also worth noting that the whole ground-state energy can be written just in terms of the Green's function using the so-called Galitskii-Migdal formula [36] (see [15] for more details)

$$E_0 = \int d\mathbf{r} d\mathbf{r}' \int_{-\infty}^{\mu} \frac{d\omega}{2\pi} \left\{ \left[-\frac{1}{2m} \nabla_{\mathbf{r}'}^2 + v(\mathbf{r}') + \omega \right] \right.$$
$$\left. Im g(\mathbf{r}, \mathbf{r}', \omega) \delta(\mathbf{r} - \mathbf{r}') \right\}. \tag{36}$$

This means that when constructing approximations for determining the single-particle Green function, the self-consistency procedure should be performed between solutions corresponding to the functional Eq. (30) and the Luttinger–Ward–Kadanoff–Baym dynamic variational method. Various approximations for calculating the single-particle Green function are presented in Refs. [9–17], including the relation with the RDMFT and DMFT. It is clearly seen from Eq. (36) that the ground state energy of the inhomogeneous system of interacting electrons, satisfying the thermodynamic limit, is uniquely defined by the single-particle Green function. As it is easy to verify, in the case of noninteracting electrons and in the self-consistent Hartree-Fock approximation, when under the condition $\omega < \mu$

$$Im g(\mathbf{r}, \mathbf{r}', \omega) = \pi \sum_{\varepsilon_{0,k} < \mu} \varphi_{0k}^*(\mathbf{r}') \varphi_{0k}(\mathbf{r}) \delta(\omega - \varepsilon_{0k}) \tag{37}$$

(see Eq. (32)), to determine the ground state energy of the inhomogeneous system of electrons, it is sufficient to know the reduced density matrix $\gamma(\mathbf{r}, \mathbf{r}')$ (see Eq. (33)). This circumstance can be used to describe the inhomogeneous system of interacting electrons, considering it as a system of weakly interacting quasiparticles, as is the case in the Landau-Silin theory for the homogeneous Fermi liquid [37, 38]. In this case, as shown in [39], the ground state energy

of the homogeneous system of interacting electrons is a functional of the reduced density matrix. To determine such a functional for the inhomogeneous system of interacting electrons, the wave-function approach to the Gibbs grand-canonical ensemble has been proposed in [17], which minimizes the Gibbs grand potential, expressed as a functional of many-particle wave functions in Fock space and their probabilities. However, the applicability of the Landau-Silin theory are violated for strongly correlated Fermi systems (see [40] and references therein).

4. Conclusions

Thus, in general case, the ground state of the inhomogeneous electronic system in the static external field, which corresponds to the thermodynamic limit, is completely defined by the single-particle Green function. Only after its calculation, the inhomogeneous density and the ground state energy of the system under consideration can be determined.

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