

Density functional, density matrix functional, and the virial theoremV. B. Bobrov,^{1,*} S. A. Trigger,^{1,2,†} and Yu. P. Vlasov³¹*Joint Institute for High Temperatures, Russian Academy of Sciences, Izhorskaya St., 13, Bd. 2. Moscow 125412, Russia*²*Institut für Physik, Humboldt-Universität zu Berlin, Newtonstraße 15, D-12489 Berlin, Germany*³*State Academy of Transport Communications, Obraztsov St. 9 127994 Moscow, Russia*

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On the basis of the virial theorem for finite motion of interacting electrons in a static external field, it is shown that ground-state energy is determined evidently by the one-particle density matrix. The exact expression for ground-state energy is found and can be applied to various problems, in particular, in studying the electronic structure of atoms, molecules, and other bound complexes.

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At present, for theoretical consideration of the equilibrium properties of inhomogeneous electron gas in a static Coulomb field of nuclei, the density-functional theory (DFT) (see, e.g., [1,2] and references therein) and the density-matrix-functional theory (DMFT) (see, e.g., [3,4] and references therein) are used. The DFT is based on the Hohenberg-Kohn theorem [5] for the ground-state energy in a local external field, while the DMFT is based on the Gilbert theorem [6] for the ground-state energy in a nonlocal static external field.

As shown in [7,8], the Hohenberg-Kohn theorem can also be proved for the one-particle density matrix $\rho^{(1)}(\mathbf{r}, \mathbf{r}_1)$ in the local external field, taking into account the fact that the nonuniform density $n(\mathbf{r}) = \rho^{(1)}(\mathbf{r}, \mathbf{r})$ is completely defined if the one-particle density matrix is known (the reverse is, generally speaking, incorrect). Within the DFT, the nonuniform density $n(\mathbf{r})$ calculation is reduced to solving the Kohn-Sham equations [9] with a local effective external field. In turn, the one-particle density matrix $\rho^{(1)}(\mathbf{r}, \mathbf{r}_1)$ calculation within the DMFT is reduced to solving the equations similar to the Hartree-Fock equations, with nonlocal effective external field (see, e.g., [3]). In this case, it seems impossible to establish a correspondence between Kohn-Sham and Hartree-Fock equations [10,11], except for the case of the quasiclassical approximation, when the ground-state energy of the inhomogeneous electron gas in the Hartree-Fock approximation is reduced to the Thomas-Fermi approximation (see, e.g., [12]). Thus, the theory of the equilibrium inhomogeneous electron gas contains an ambiguity associated with the choice between DFT and DMFT. Such an ambiguity can be resolved in two possible ways. Either both theories lead to equivalent results for the ground-state energy of the inhomogeneous electron gas or the choice between them is caused by characteristics of the local external field acting on the electron gas.

Let us pay attention to the fact that the theoretical study of properties of equilibrium systems of interacting particles is often based on the assumption that the system Hamiltonian completely defines these properties (see, e.g., [13]). However, setting the Hamiltonian of the system is insufficient to correctly describe its equilibrium properties. A typical example is the “special” (in addition to the Hamiltonian) consideration of the identity of particles in the nonrelativistic consideration

of quantum equilibrium systems, which necessitates the procedure of wave-function symmetrization (or antisymmetrization) or the use of the secondary quantization formalism (see, e.g., [14]). To solve the problem under consideration, it is required to know boundary conditions for wave functions, without which the Schrödinger equation with an exact Hamiltonian of the interacting particle system cannot be solved [14]. The conventional quantum-mechanical statement of the problem about boundary conditions is reduced to the condition of wave function vanishing at an infinite distance of a particle from the “force center” (an alternative problem statement in which a particle at an infinite distance behaves as a free one relates to the scattering theory, and it obviously cannot be used in describing equilibrium properties). It is the case of the so-called finite motion, i.e., motion in a limited region of space, although the space itself is not limited in any way. According to quantum-mechanical concepts, stationary states of the many-particle system with discrete energy spectrum correspond to finite motion [14]. Among such problems is the major problem of the determination of bound electronic states in a static field of nuclei (atom, molecule, etc.). In turn, the so-called virial theorem, which was established 140 years ago by Clausius within classical mechanics, is valid for the finite motion.

The virial theorem formulation for quantum mechanics, taking into account vanishing wave functions at infinity, is given by (see, e.g., [15])

$$2\langle K \rangle - \langle \mathbf{r} \cdot \nabla U(\mathbf{r}) \rangle = 0, \quad (1)$$

where angle brackets $\langle \dots \rangle$ denote, as usual, quantum-mechanical or quantum-statistical averaging (depending on the problem statement), K is the kinetic energy operator, $\mathbf{r} \cdot \nabla U(\mathbf{r})$ is the potential energy virial, and the quantity U is the sum of potential energies of the interparticle interaction U^{int} with potential φ^{int} and the energy of the interaction U^{ext} with the static external field with potential φ^{ext} which provides finite motion of particles in the considered equilibrium system of N interacting particles:

$$U = U^{\text{int}} + U^{\text{ext}}, \quad U^{\text{int}} = \frac{1}{2} \sum_{a,b=1, a \neq b}^N \varphi^{\text{int}}(|\mathbf{r}_a - \mathbf{r}_b|), \quad (2)$$

$$U^{\text{ext}} = \sum_{a=1}^N \varphi^{\text{ext}}(\mathbf{r}_a).$$

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Let us pay attention to the fact that the virial theorem derivation [15] for quantum mechanics is based on analysis of the stationary Schrödinger equation for the system of interacting electrons in the Coulomb field of immobile nuclei and is used for describing the bound (localized) electronic states in the ground energy state. Due to the exponential decay of localized wave functions of bound electronic states with the distance from nuclei being localization centers, wave functions can be taken equal zero at the system boundaries. A detailed analysis (see [16] and references therein) shows that the virial theorem formulation for the ground state in the “traditional” form (1) requires that not only wave functions themselves, but also their spatial derivatives, would vanish at infinity. This is exactly the consideration of the boundary conditions for solving the corresponding Schrödinger equation. It is easy to verify, e.g., that relation (1) is satisfied for one electron in the Coulomb field of the attractive center. In what follows, we take into account that in the secondary quantization representation,

$$\begin{aligned} \langle \mathbf{r} \cdot \nabla U^{\text{ext}}(\mathbf{r}) \rangle &= \int n(\mathbf{r})[\mathbf{r} \cdot \nabla \varphi^{\text{ext}}(\mathbf{r})] d\mathbf{r}, \\ n(\mathbf{r}) &= \langle N(\mathbf{r}) \rangle, \quad N(\mathbf{r}) = \Psi^\dagger(\mathbf{r})\Psi(\mathbf{r}), \end{aligned} \quad (3)$$

where $n(\mathbf{r})$ is the inhomogeneous density of the number of particles, $\Psi^\dagger(\mathbf{r})$ and $\Psi(\mathbf{r})$ are the field creation and annihilation operators, and $N(\mathbf{r})$ is the density operator of the number of particles. Integrating in (3) by parts, it is easy to verify that

$$\int n(\mathbf{r})[\mathbf{r} \cdot \nabla \varphi^{\text{ext}}(\mathbf{r})] d\mathbf{r} = - \int \{3n(\mathbf{r}) + \mathbf{r} \cdot \nabla n(\mathbf{r})\} \varphi^{\text{ext}}(\mathbf{r}) d\mathbf{r}. \quad (4)$$

In deriving (4), it was taken into account that the inhomogeneous density for finite motion vanishes on the infinitely remote surface bounding the space occupied by the system (the so-called condition at infinity [14]). In this case,

$$\oint n(\mathbf{r}) \varphi^{\text{ext}}(\mathbf{r}) \mathbf{r} \cdot d\mathbf{S} = 0, \quad (5)$$

where $d\mathbf{S} = \mathbf{n}dS$, \mathbf{n} is the unit vector of the external normal to the surface, and dS is the infinitely remote surface unit. Therefore, for the exact solution to the Schrödinger equation in the static Coulomb field of nuclei, which provides finite motion for the system of interacting electrons in the ground localized state (atom, molecule, etc.) in infinite space, which is of major interest for quantum chemistry, the virial theorem (1), taking into account (2) and (4), takes the form

$$2\langle K \rangle + \langle U \rangle = - \int \{2n(\mathbf{r}) + \mathbf{r} \cdot \nabla n(\mathbf{r})\} \varphi^{\text{ext}}(\mathbf{r}) d\mathbf{r}. \quad (6)$$

Hence, according to (2), for the ground-state energy E_0 of such a system,

$$E_0 = \langle K \rangle_0 + \langle U \rangle_0, \quad \langle U \rangle_0 = \langle U^{\text{int}} \rangle_0 + \langle U_0^{\text{ext}} \rangle, \quad (7)$$

one finds the equality

$$E_0 = -\langle K \rangle_0 - \int \{2n_0(\mathbf{r}) + \mathbf{r} \cdot \nabla n_0(\mathbf{r})\} \varphi^{\text{ext}}(\mathbf{r}) d\mathbf{r}, \quad (8)$$

where the index 0 means that the corresponding quantity is defined for the ground state of the system. Note that

a relation similar to (8) has been used (see, e.g., [17,18]) in parallel with the Hellman-Feynman theorem, to analyze the universal density functional in the framework of the Hohenberg-Kohn hypothesis [5] on the existence of a universal density functional (for more detail see [19]). Take into account the fact that the average kinetic energy is completely defined by the one-particle density matrix $\rho^{(1)}(\mathbf{r}_1, \mathbf{r}_2) = \langle \Psi^\dagger(\mathbf{r}_1)\Psi(\mathbf{r}_2) \rangle$,

$$\langle K \rangle = -\frac{\hbar^2}{2m} \int \{ \nabla_{\mathbf{r}_1}^2 \rho^{(1)}(\mathbf{r}, \mathbf{r}_1) \}_{|_{\mathbf{r}_1=\mathbf{r}}} d\mathbf{r}. \quad (9)$$

In turn, the inhomogeneous density of the number of particle is $n(\mathbf{r}) = \rho^{(1)}(\mathbf{r}, \mathbf{r})$. Hence, according to (8) and (9), the ground-state energy of the system of interacting electrons in the static Coulomb field of nuclei during finite motion is completely defined by the one-particle density matrix.

Taking into account the Hohenberg-Kohn theorem for the one-particle density matrix [7,8], we come to the conclusion that the ground-state energy of the inhomogeneous interacting electron gas during finite motion is undoubtedly the one-particle density matrix functional. Strictly speaking, this does not mean that the ground-state energy cannot be the density functional in this case. In this regard, let us pay attention to the fact that in the case of noninteracting electrons ($\langle U^{\text{int}} \rangle = 0$), according to (6), we can write

$$\langle K \rangle = -\frac{1}{2} \int \{3n(\mathbf{r}) + \mathbf{r} \cdot \nabla n(\mathbf{r})\} \varphi^{\text{ext}}(\mathbf{r}) d\mathbf{r}. \quad (10)$$

Hence, taking into account (8) and (10), the ground-state energy for noninteracting particles during finite motion in a given static local field can be considered as both the density matrix functional and the density functional.

Thus, based on (8) and (9), we can certainly argue that, in the case of finite motion of interacting electrons in a static external field, the ground-state energy is completely determined by the one-particle density matrix. This means that the results of the use of the DMFT have an advantage over the results of the use of the DFT, in particular, in studying the electronic structure of atoms, molecules, and other bound complexes, where interacting electrons exhibit finite motion. It is obvious, since the explicit form of the density functional is unknown. However, Eq. (8) cannot be directly applied to the determination of the one-particle density matrix using the variational procedure. To use the variational procedure, as in the case of the DFT (see [19] for more details), the existence of the universal (i.e., whose form is the same for various external fields) functional of the one-particle density matrix should be proved. The existence of such a universal functional of the one-particle density matrix is one of the central problems of the DMFT (see, e.g., [20]). In addition, to use (8) for a variational procedure the detailed consideration of the N -representation problem is needed. Nevertheless, the existence of the exact DMFT functional [(8) and (9)] already provides the basis for many practical applications.

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