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BRIEF COMMUNICATIONS

CLAUSIUS VIRIAL THEOREM AND SCALE RELATIONS IN THE METHOD OF MANY-PARTICLE DENSITY FUNCTIONALS

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Scale relations that appear in applying the method of many-particle density functionals are considered. Scale transformation is applied to obtain the relations for the kinetic energy functionals and for the potential energy of interparticle interactions and for the interactions of particles with an external field for the ground states of the systems of charged particles in a pure Coulomb field. The Clausius virial theorem for the method of many-particle density functionals has been formulated.

Scale transformations in the single-particle method of density functionals attracted attention as early as in the 1950s, when Gombash reported the results (see, e.g., [1]) obtained within the framework of the Thomas–Fermi model. Similar studies were performed with the use of more strict theories based on the Hoenberg–Konn–Sham formalism [2]. Examining the scale relations that appear in the theory of many-particle density functionals [3, 4] is of most interest. The theory is based on the description of N-particle quantum systems with the use of many-particle density functions $n_m(\mathbf{r}_1, \ldots, \mathbf{r}_m)$ defined as the diagonal elements of m-particle density matrices normalized to $C_N^m = \dfrac{N!}{m!(N-m)!}$ and independent of spin. By the generalized Hoenberg–Konn theorem, the total energy E_0 of the ground state of a Fermi system is the single-particle functional $n_m(\mathbf{r}_1, \ldots, \mathbf{r}_m)$, which reaches a minimum for the function describing the spatial distribution of particles in the ground state. The Hamiltonian of the system is also uniquely determined by the m-particle density function $H = H[n_m]$.

Consider the wave function $\psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ normalized to unity and corresponding to the ground state of the system with the Hamiltonian

$$H = T + V + W\,, \tag{1}$$

where

$$T = \sum_{i=1}^{N} \left(-\frac{1}{2}\Delta_i\right), \quad V = \sum_{i=1}^{N} V(\mathbf{r}_i), \quad W = \sum_{i=2}^{N} \sum_{j<i}^{N-1} W(\mathbf{r}_i, \mathbf{r}_j)\,.$$

The function $\psi[\gamma](\mathbf{r}_1, \ldots, \mathbf{r}_N) = \gamma^{3N/2}\psi(\gamma\mathbf{r}_1, \ldots, \gamma\mathbf{r}_N)$ is also normalized to unity. According to the Rayleigh–Ritz principle, $\dfrac{d}{d\gamma}\langle\psi[\gamma]|H|\psi[\gamma]\rangle|_{\gamma=1} = 0$. If the Hamiltonian H corresponds to a system of charged particles moving in a pure Coulomb field, then using the scale properties of the operators T, V, and W, we can easily obtain the scale relations $\langle\psi[\gamma]|T|\psi[\gamma]\rangle = \gamma^2\langle\psi|T|\psi\rangle$, $\langle\psi[\gamma]|V|\psi[\gamma]\rangle = \gamma\langle\psi|V|\psi\rangle$, and $\langle\psi[\gamma]|W|\psi[\gamma]\rangle = \gamma\langle\psi|W|\psi\rangle$, which imply the well-known Clausius virial theorem for Coulomb systems [2]

$$2\langle\psi|T|\psi\rangle = -\langle\psi|V|\psi\rangle - \langle\psi|W|\psi\rangle\,.$$

If the function $\psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ of the ground state of a system with Hamiltonian (1) is responsible for the m-particle density function $n_m(\mathbf{r}_1, \ldots, \mathbf{r}_m)$, then the m-particle density function $n_m[\gamma](\mathbf{r}_1, \ldots, \mathbf{r}_m) = \gamma^{3m} n_m(\gamma\mathbf{r}_1, \ldots, \gamma\mathbf{r}_m)$ will correspond to the scale transformed function $\psi[\gamma](\mathbf{r}_1, \ldots, \mathbf{r}_N)$.

The generalized Hoenberg–Konn theorem implies that in the ground state, the kinetic energy and the potential energy of the system particles interactions with each other and with an external field are the single-valued universal functionals of the m-particle density function of the ground state

$$T[n_m] = \langle\psi[n_m]|T|\psi[n_m]\rangle\,, \quad V[n_m] = \langle\psi[n_m]|V|\psi[n_m]\rangle\,, \quad W[n_m] = \langle\psi[n_m]|W|\psi[n_m]\rangle\,.$$

According to the Rayleigh–Ritz principle,

$$T[n_m[\gamma]] + V[n_m[\gamma]] + W[n_m[\gamma]] = \inf\langle\varphi[n_m[\gamma]]\,|T + V[n_m[\gamma]] + W[n_m[\gamma]]|\,\varphi[n_m[\gamma]]\rangle\,,$$

where $\varphi[n_m[\gamma]]$ is any wave function of the ground state of an N-fermion system with the Hamiltonian $H[n_m[\gamma]]$, leading to the m-particle density function $n_m[\gamma](\mathbf{r}_1, \ldots, \mathbf{r}_m)$. The form of $H[n_m[\gamma]]$ can be determined from the following considerations. Since $H[n_m[\gamma]] = H$ and $\varphi[n_m[\gamma]] = \psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ for $\gamma = 1$, we can obtain the Schrödinger equation for the function $\psi[\gamma](\mathbf{r}_1, \ldots, \mathbf{r}_N)$

$$E\psi[\gamma](\mathbf{r}_1, \ldots, \mathbf{r}_N) = H(\gamma\mathbf{r}_1, \ldots, \gamma\mathbf{r}_N)\,\psi[\gamma](\mathbf{r}_1, \ldots, \mathbf{r}_N)\,.$$

This equation can be transformed to

$$(T + \gamma U + \gamma W)\psi[\gamma](\mathbf{r}_1, \ldots, \mathbf{r}_N) = (\gamma^2 E)\psi[\gamma](\mathbf{r}_1, \ldots, \mathbf{r}_N)\,. \tag{2}$$

In other words, $\psi[\gamma](\mathbf{r}_1, \ldots, \mathbf{r}_N)$ is the wave function of the ground state of the N-fermion system which leads to the m-particle density function $n_m[\gamma](\mathbf{r}_1, \ldots, \mathbf{r}_m)$. Since the Hamiltonian of the system is uniquely determined by the m-particle density function of the ground state, (2) implies that

$$H[n_m[\gamma]] = T + \gamma V + \gamma W \quad \text{and} \quad \varphi[n_m[\gamma]] = \psi[\gamma]\,.$$

Hence,

$$T[n_m[\gamma]] = \langle\varphi[n_m[\gamma]]|T|\varphi[n_m[\gamma]]\rangle = \langle\psi[\gamma]|T|\psi[\gamma]\rangle = \gamma^2 T[n_m]\,;$$
$$V[n_m[\gamma]] = \langle\varphi[n_m[\gamma]]|V[n_m[\gamma]]|\varphi[n_m[\gamma]]\rangle = \langle\psi[\gamma]|\gamma V|\psi[\gamma]\rangle = \gamma V[n_m]\,;$$
$$W[n_m[\gamma]] = \langle\varphi[n_m[\gamma]]|W[n_m[\gamma]]|\varphi[n_m[\gamma]]\rangle = \langle\psi[\gamma]|\gamma W|\psi[\gamma]\rangle = \gamma W[n_m]\,.$$

Thus, for many-particle density functionals, the Rayleigh–Ritz principle also implies that $2\langle\psi|T|\psi\rangle = -\langle\psi|V|\psi\rangle - \langle\psi|W|\psi\rangle$, whence $2T[n_m] = -V[n_m] - W[n_m]$.

Note that in the single-particle theory of Hoenberg–Konn–Sham density functionals, the scale relations between the total energy components differ essentially from the obtained ones [5]

$$T[n_1[\gamma]] < \gamma^2 T[n_1] \quad \text{for} \quad \gamma > 1; \qquad T[n_1[\gamma]] > \gamma^2 T[n_1] \quad \text{for} \quad \gamma < 1;$$
$$V[n_1[\gamma]] = \gamma V[n_1] \quad \text{for any} \quad \gamma;$$
$$W[n_1[\gamma]] > \gamma W[n_1] \quad \text{for} \quad \gamma > 1; \qquad W[n_1[\gamma]] < \gamma W[n_1] \quad \text{for} \quad \gamma < 1,$$

and only for noninteracting particles, $T[n_1[\gamma]] = \gamma^2 T[n_1]$. Indeed, according to a less strict classical Hoenberg–Konn theorem, which is the base of the single-particle approach, introducing the function $n_1(\mathbf{r})$, we determine the Hamiltonian of the system accurate to W rather than uniquely. For this reason, the Clausius virial theorem is of limited applicability in the single-particle Hoenberg–Konn–Sham method, while in the many-particle theory of density functionals, these limitations are removed.

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