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Virial theorem for an inhomogeneous medium, boundary conditions for the wave functions, and stress tensor in quantum statistics

V. B. Bobrov, P. A. Trigger, J. F. van Heijst, and P. P. J. M. Schram

Joint Institute for High Temperatures, Russian Academy of Sciences, Izhorskaya Street 13, Building 2, 125412 Moscow, Russia
Eindhoven University of Technology, P.O. Box 513, MB 5600 Eindhoven, The Netherlands

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On the basis of the stationary Schrödinger equation, the virial theorem in an inhomogeneous external field for the canonical ensemble is proved. It is shown that the difference in the form of virial theorem is conditioned by the value of the wave-function derivative on the surface of the volume, surrounding the system under consideration. The stress tensor in such a system is determined by the average values of the wave-function space derivatives.

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Exact relations for describing equilibrium systems of interacting particles are of fundamental importance. Among such exact relations is the so-called virial theorem established by Clausius more than 130 years ago (see, e.g., [1–4]). In the original formulation of classical mechanics [1,2], the virial theorem relates the time-average values of kinetic and potential energies,

\[ 2\langle K \rangle - \langle r \cdot \nabla U(r) \rangle = 0, \]  

where \( \langle K \rangle \) is the average kinetic energy and \( \langle r \cdot \nabla U(r) \rangle \) is the average virial of the potential energy. From the condition of the equivalence of time and statistical averaging [3], it follows that the virial theorem should also be satisfied for statistical description of matter [3,4]. In this case, there is an important observation [2] to which no proper significance is often attached. The essence of this observation is reduced to that the virial theorem is valid if the particle motion in the system occurs in a bounded region of space [2]. For the statistical description of the equilibrium system of interacting particles, such a bounded region of space characterizes a volume occupied by the system under consideration [3] and, in the thermodynamic limit, leads to the pressure quantity appearing in the virial theorem when considering the classical system within the canonical ensemble (see, e.g., [4]).

Thus, it can be argued that the virial theorem formulation is substantially related to the consideration of a very large but limited volume occupied by the system, thus, to the conditions on the surface bounding this volume. At the same, putting into consideration a large but finite volume occupied by the system is equivalent [5] to placing the system under study into a certain external field characterized by “surface” forces. The case in point is the external field acting on the system under consideration in a “narrow” layer near the surface bounding the system volume. We further assume that a linear size of such a layer is much smaller than all characteristic “internal” sizes of the system under study. Then, in the thermodynamic limit, this inhomogeneous surface layer can be set to zero, and the model system can be considered in a “box” with a specified large but finite volume with infinite potential walls such that system particles cannot leave this volume [5]. It is clear that such a model corresponds to the statistical consideration of a set number of interacting particles in a given volume within the canonical ensemble [3–5]. On the other hand, the presence of the external field causes inhomogeneity of the system under consideration, which necessitates the consideration of internal stresses [6]. In this case, from general considerations, the virial theorem takes the form [7]

\[ 2\langle K \rangle - \langle r \cdot \nabla U(r) \rangle = -\oint x_r t_{\alpha \beta} dS_{\beta}, \]

where \( t_{\alpha \beta} \) is the stress tensor, \( dS = n dS \), \( n \) is the unit vector of the outward normal to the surface, and \( dS \) is the surface element bounding the given volume. It is clear that similar relations take place for the quantum-mechanical description of the system of interacting particles, which follows, in particular, from the correspondence principle [8].

In this case, it is quite reasonable that the question arises about the relation between Eqs. (1) and (2), since the fundamental difference between the right-hand sides of equalities (1) and (2) cannot be explained only by statistical averaging. To solve this problem, it is necessary to derive the virial theorem, based on the microscopic description of the equilibrium system in a bounded volume, taking into account boundary effects on the surface. In this sense, the quantum-mechanical description seems to be preferable since it implies the existence of boundary conditions for wave functions.

The virial theorem for quantum mechanics was apparently formulated for the first time in Slater’s paper [9] (see also [1,10]), based on an analysis of the stationary Schrödinger equation for a system of interacting electrons in the Coulomb field of stationary nuclei, and was applied to describe bound (localized) electronic states in the ground state. In this case, due to the exponential decay of wave functions of bound electronic states with distances from the nuclei being localization centers, these wave functions are considered to be equal to zero at system boundaries. Slater’s paper [9] was analyzed in detail in [11–13]. It was shown that the virial theorem formulation for the ground state in the “conventional” form requires that not only the wave functions them-
selves, but also their spatial derivatives would become zero at the boundary of the system under consideration.

In this regard, let us consider an equilibrium system of $N$ interacting particles of the same type with mass $m$, which are in a very large but finite volume $V$ with infinite potential walls, which is bounded by the surface $S$. Let the wave function $\psi(\{r_a\})$, which depends on the coordinates $r_a$ ($a=1, \ldots, N$) of all particles of the system under study, be symmetrized (or antisymmetrized) taking into account the particle identity [8], characterizes the state of this system with energy $E$, and satisfies the stationary Schrödinger equation [8], as well as the complex-conjugate wave function $\psi^*$,

$$\sum_{a=1}^{N} \left( -\frac{\hbar^2}{2m} \Delta_a \psi \right) + (U-E) \psi = 0,$$

$$\sum_{a=1}^{N} \left( -\frac{\hbar^2}{2m} \Delta_a \psi^* \right) + (U-E) \psi^* = 0. \quad (3)$$

The quantity $U$ is the sum of potential energies of the inter-particle interaction $U^{\text{int}}$ with the potential $\varphi^{\text{int}}$ and the interaction with the static external field $U^{\text{ext}}$ with the potential $\varphi^{\text{ext}}$, which characterizes “volume” external forces (e.g., the external gravitational field),

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

$$U^{\text{ext}} = \sum_{a=1}^{N} \varphi^{\text{ext}}(r_a). \quad (4)$$

According to [9], we differentiate the first equation in Eqs. (3) with respect to the variable $r_b$ and multiply it scalarly by $r_b \psi^*$; then we take into account the second equation in Eqs. (3), but—in contrast to the procedure used in [9]—we will not sum over the particle index $b$. As a result, we obtain

$$-\frac{\hbar^2}{2m} \sum_{a=1}^{N} \{ \psi^* (r_b \cdot \nabla_a \Delta_a \psi) - \Delta_a \psi^* (r_b \cdot \nabla_a \psi) \} + |\psi|^2 (r_b \cdot \nabla_a U) = 0. \quad (5)$$

Then we integrate equality (5) over all coordinates $r_a$ of all particles over the entire volume $V$. Integration of the second term, taking into account Eq. (4), yields the average quantum-mechanical value of the virial of forces acting on particle $b$ from the side of other particles and the external field,

$$|\psi|^2 (r_b \cdot \nabla_a U) \rightarrow \langle \psi^* (r_b \cdot \nabla_a U) \rangle,$$

$$U^{(l)}(r_b) = \sum_{a=1,a\neq b}^{N} \varphi^{\text{int}}(|r_a - r_b|) + \varphi^{\text{ext}}(r_b). \quad (6)$$

where angular brackets $\langle \cdots \rangle$ mean quantum-mechanical averaging with wave functions $\psi^*$ and $\psi$ [8]. To the first term in Eqs. (3), we apply integration by parts. In this case, integration over all other coordinates, except for $r_a$, does not affect the result. We take into account that the system under consideration is in the volume with infinite potential walls. Therefore, the wave functions $\psi^*$ and $\psi$ vanish once at least one of the coordinates of any particle appears at the boundary of the volume $V$ under consideration, i.e., on the surface $S$,

$$[\psi^*]_{r_b \rightarrow S} = [\varphi]_{r_b \rightarrow S} = 0,$$

$$[\nabla_a \psi^*]_{r_b \rightarrow S} = [\nabla_a \varphi]_{r_b \rightarrow S} = 0 \quad (\alpha \neq b). \quad (7)$$

Here, the square brackets with subscript $r_b \rightarrow S$ mean that the bracketed function is defined at the coordinate $r_b$ on the surface $S$ bounding the volume $V$. In this case, the derivatives of wave functions $\psi^*$ and $\psi$ on the surface $S$ with identical particle indices, generally speaking, do not vanish,

$$[\nabla_b \psi^*]_{r_b \rightarrow S} \neq 0, \quad [\nabla_b \varphi]_{r_b \rightarrow S} \neq 0. \quad (8)$$

Thus, taking into account Eqs. (7) and (8), we find

$$\int \{ \psi^* \nabla_b (\Delta_a \psi) - \Delta_a \psi^* (r_b \cdot \nabla_a \psi) \} dV_a = -\left\{ 2 \int \psi^* \Delta_a \psi dV_a + \oint (r_b \cdot \nabla_a \psi^* (r_b \cdot \nabla_a \psi) dS_a) \right\} \delta_{a,b}. \quad (9)$$

Then we put into consideration the one-particle density matrix $R^{(1)}(r_{1b}, r_{2b})$ for particle $b$, which is defined by integration over all coordinates, except for the coordinate of separated particle $b$, the product of the wave function $\psi (r_{1b}, \{r_a\})$, and the complex-conjugate wave function $\psi^* (r_{1b}, \{r_a\})$. Then the second term on the right-hand side of Eq. (9) after quantum-mechanical averaging takes the form

$$\oint (r_b \cdot \nabla_b \psi)(\nabla_b \psi^* \cdot dS_b) \rightarrow \oint (r_{1b} \cdot \nabla_{1b})(\nabla_{1b} \cdot dS_{1b}) \times R^{(1)}(r_{1b}, r_{2b})_{r_{1b}=r_{2b}=S}. \quad (10)$$

Thus, after the procedure of quantum-mechanical averaging, it directly follows from Eqs. (5)–(10) that the equality

$$2\langle K^{(1)} \rangle - \langle r_1 \nabla_1 U^{(l)}(r_1) \rangle = \frac{\hbar^2}{2m} \oint (r_2 \cdot \nabla_2)(\nabla_1 \cdot dS_1) \times R^{(1)}(r_1, r_2)_{r_1=r_2=S} \quad (11)$$

is valid for any identical particle. Here, $K^{(1)}$ is the kinetic-energy operator for one particle. It is clear that summing over all particles in relation (11) is equivalent to multiplying by the number of particles $N$. If the right-hand side in relation (11) vanishes, which corresponds to the violation of conditions (8), we obtain the conventional form of the virial theorem (1). The violation of conditions (8) corresponds to the consideration of the particle state localized in the volume. In this case, particles of the system under study do not affect the box walls, as well as box walls do not affect the system under consideration. We also note that, according to the above consideration, relation (11) is also valid for multi-component systems, taking into account indexing of distinct-
tive features of particles of various types, e.g., particle masses.

Now let us pay attention that the above consideration equally relates to wave eigenfunctions $\psi_\alpha$ and eigenenergies $E_\alpha$ of the Hamiltonian of the equilibrium system of interacting particles in a given volume $V$ in the static external field. This means that averaging over the canonical ensemble can be performed in relation (11). As a result, after summing over all particles and passing to the thermodynamic limit, relation (2) directly follows from Eq. (11), in which the stress tensor $t_{\alpha\beta}$ per particle is defined by the equality

$$t_{\alpha\beta}(\mathbf{r}) = -\frac{\hbar^2}{2m} \left[ \nabla_{\alpha\beta} R^{(1)}(\mathbf{r}_1, \mathbf{r}_2) \right]|_{\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}},$$  \hspace{1cm} (12)

where $R^{(1)}(\mathbf{r}_1, \mathbf{r}_2)$ is the one-particle density matrix in quantum statistics [3,4], which is determined by averaging of the quantum-mechanical density matrix $R^{(1)}(\mathbf{r}_1, \mathbf{r}_2)$ over the canonical ensemble.

In the absence of external volume forces, $\varphi^{(v)}=0$, the stress tensor $t_{\alpha\beta}$ characterizes uniform compression strains directly related to the pressure $P$ in the system under study [6]. In this case, the stress tensor is written as $t_{\alpha\beta} = -P \delta_{\alpha\beta}$ [6]. Then, taking into account Eqs. (2) and (12), and the pressure constancy as the condition of thermodynamic equilibrium of a homogeneous system [3], the virial theorem takes the form

$$2\langle K \rangle - \langle \mathbf{r} \cdot \nabla U(\mathbf{r}) \rangle = 3PV.$$  \hspace{1cm} (13)

A similar result can be obtained within the quantum-statistical description of a homogeneous system directly from the thermodynamic definition of the pressure (see, e.g., [4]). Thus, the difference of formulations (1) and (2) of the virial theorem is caused by different values of the spatial derivative of the wave function of the system of interacting particles on the surface bounding the volume of the system under consideration.

It is necessary to emphasize that in applications to solid state the traditional derivation of the virial theorem is based on a “stretch” of wave functions by transformation of each particle coordinate $r_{\alpha} \rightarrow r_{\alpha} + \sum \varepsilon_{\alpha\beta} r_{\beta}$, where $\varepsilon_{\alpha\beta}$ is a symmetric (i.e., rotation-free) strain tensor [15,16]. To find the virial theorem in this case the variational principle with respect to $\varepsilon_{\alpha\beta}$ is used (see [17,18], and the references in these papers). However, within such an approach, the effects connected with the boundary conditions for the wave functions, which are taken into account in the present Rapid Communication, cannot be found. This statement follows from the fact that in the traditional theory of solids the boundary conditions for the wave functions are periodic [19], which is connected with the periodic structure of ideal lattices.

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