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A generalized quantum virial equation

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Abstract. A method, similar to the one previously used by the author in his derivation of a generalized classical virial theorem, is used to derive a generalized quantum virial equation. This equation is applicable to any part of a larger system of particles. Furthermore, by the introduction of a flux density operator, it is possible to express the quantum surface flux virial in two alternative forms, as easily interpreted as the classical form. As an intermediate result, an equation of continuity for a general one-particle observable is obtained. In an appendix, an equation of motion of the reduced density matrix of the first order is derived.

1. Introduction

The classical and quantum virial theorems, as originally derived by Clausius (1870), Fock (1930) and Slater (1933), are only applicable to petit ensembles (i.e. fixed number of particles), subject to no net external action. As a consequence, these theorems are not, in general, applicable to limited parts of a larger system, since such parts are mostly represented by grand ensembles (i.e. fluctuating number of particles). In a preceding paper (Schweitz 1977), the present author has derived a classical virial equation, applicable to grand ensembles subjected to non-zero external action. This 'grand' virial equation is of the form

$$2T + Z_p + Z_s = 0, \quad (1)$$

where T is the time average of the kinetic energy contents of the observed volume Ω , Z_p is the 'petit' virial

$$Z_p = \left(\sum_i \mathbf{x}_i \cdot \mathbf{F}_i \right)_{\text{time average}}, \quad (2)$$

where the summation runs over all particles instantaneously contained in Ω , and Z_s is a 'surface flux virial', caused by the exchange of particles through the (penetrable) surfaces of Ω :

$$Z_s = \oint dS \mathbf{x} \cdot (\bar{\mathbf{p}}(\mathbf{x}) - \vec{\mathbf{p}}(\mathbf{x})). \quad (3)$$

$\bar{\mathbf{p}}(\mathbf{x})$ and $\vec{\mathbf{p}}(\mathbf{x})$ are the mean momentum flux densities (momentum/time and area) into

and out of the observed volume at the point \mathbf{x} . Thus, the total flux density at \mathbf{x} is $\vec{p}(\mathbf{x}) + \vec{p}(\mathbf{x})$. \vec{p} and \vec{p} are dependent on the orientation of the surface S at \mathbf{x} . For $\vec{p} \equiv \vec{p} \equiv 0$, Z_S vanishes and equation (1) takes the form of the Clausius 'petit' virial equation.

Within quantum mechanics, however, one works with smeared-out probability densities rather than discrete point-particles. All N particles of a larger system may be considered parts of any subsystem, in the sense that all particles may have non-vanishing probability densities in the subsystem. Thus, the summation of equation (2) must be extended over all N particles of the larger system, but the corresponding probability densities are integrated only over the volume Ω of the subsystem. Similarly, in Z_S all N particles contribute to the probability densities of the momentum flux densities involved.

In the literature, some recent derivations of generalized quantum virial equations are found. In a series of papers, Bader *et al* (see Srebrenik and Bader 1974) have developed an interesting method of spatial partitioning of molecular systems into several fragments which individually satisfy one type of 'petit' virial relationship. In this method the partitioning surfaces must be chosen in a particular and well defined manner. This choice of surfaces, however, does not in general imply a vanishing surface flux virial (which would make the 'grand' equation become 'petit'). The authors evade this difficulty by choosing the origin of their reference system in a very particular manner (i.e. their theorem is not invariant under transformation). Weislinger and Olivier (1974) have derived a generalized quantum virial equation for the special case of a periodic system. All authors mentioned above have derived their equations from the Schrödinger equation, essentially by means of Slater's (1933) original method. McLellan (1974), on the other hand, has derived a virial equation from the Heisenberg equation. McLellan, however, introduces some limiting conditions on the wavefunction in the final step of his derivation, whereby his surface flux virial is reduced to a virial of constraint forces of a type first introduced by Slater (1933).

In the present work, a method, similar to the one used by the author in his derivation of the classical 'grand' virial theorem (Schweitz 1977), is used to derive a generalized quantum virial theorem. This theorem is applicable to any part of a larger system of particles. Furthermore, by the introduction of a flux density operator, it is possible to express the quantum surface flux virial Z_S in two alternative forms, as easily interpreted as the classical Z_S of equation (3). As an intermediate result, an equation of continuity for a general one-particle observable is obtained.

In the following derivations, it is tacitly implied that all wavefunctions and density matrices are time dependent. Furthermore, summation over the spin coordinates is always assumed.

2. An equation of continuity for a one-particle observable

The general idea in the derivation of the classical virial equation is to differentiate a sum of one-particle observables with respect to time, and then find the time average of the resulting derivative. Thus we introduce a general one-particle operator \hat{Z}_i , acting on the coordinates \mathbf{x}_i of the i th particle. \hat{Z}_i is assumed to be time independent. The sum of the corresponding expectation values, taken over a limited part Ω of the space, then is

$$M = \sum_{i=1}^N \int_{\Omega} dv_i \int_{-\infty}^{\infty} dv \bar{\Psi} \hat{Z}_i \Psi, \quad (4)$$

where the symbol $\int' dv$ indicates integration over all coordinates except the i th. In terms of the reduced density matrix formalism, equation (4) may be written

$$M = \int_{\Omega} dv_1 \hat{Z}_1 \gamma(\mathbf{x}_1 | \mathbf{x}'_1), \quad (5)$$

the time derivative of which is

$$\frac{dM}{dt} = \int_{\Omega} dv_1 \hat{Z}_1 \frac{\partial}{\partial t} \gamma(\mathbf{x}_1 | \mathbf{x}'_1). \quad (6)$$

To eliminate $\partial\gamma/\partial t$ from equation (6), an equation of motion for γ is needed. Such an equation is easily derived from the time-dependent Schrödinger equation, and may be expressed as

$$-\frac{\hbar^2}{2m}(\Delta_1 - \Delta'_1)\gamma(\mathbf{x}_1 | \mathbf{x}'_1) + N \int'_{\infty} dv (V - V')\bar{\Psi}'\Psi = i\hbar \frac{\partial}{\partial t} \gamma(\mathbf{x}_1 | \mathbf{x}'_1). \quad (7)$$

Primed operators act only on primed coordinates, V and Ψ are functions of unprimed coordinates while V' and Ψ' are functions of one primed (\mathbf{x}'_1) and remaining unprimed coordinates ($\mathbf{x}_2, \mathbf{x}_3, \dots$). It is also possible to express the second term of equation (7) in terms of density functions (see appendix), whereby the following derivations could be carried through without the use of complete wavefunctions. For convenience, however, we choose to introduce density functions in this term at a later stage. Thus, equation (6) may be written

$$\frac{dM}{dt} = \frac{i\hbar}{2m} \int_{\Omega} dv_1 \hat{Z}_1 (\Delta_1 - \Delta'_1)\gamma(\mathbf{x}_1 | \mathbf{x}'_1) + \frac{N}{i\hbar} \int_{\Omega} dv_1 \int'_{\infty} dv \hat{Z}_1 (V - V')\bar{\Psi}'\Psi. \quad (8)$$

If, in the first integrand, $\Delta_1 \hat{Z}_1 \gamma$ is first added and then subtracted, one obtains

$$\frac{dM}{dt} = \frac{i\hbar}{2m} \int_{\Omega} dv_1 (\Delta_1 - \Delta'_1) \hat{Z}_1 \gamma + \frac{i\hbar}{2m} \int_{\Omega} dv_1 [\hat{Z}_1, \Delta_1] \gamma + \frac{N}{i\hbar} \int_{\Omega} dv_1 \int'_{\infty} dv \hat{Z}_1 (V - V')\bar{\Psi}'\Psi. \quad (9)$$

In the second integrand, the ordinary commutator notation is used. By means of Green's first identity, the first volume integral is transformed into a surface integral:

$$\int_{\Omega} dv_1 (\Delta_1 - \Delta'_1) \hat{Z}_1 \gamma \rightarrow \oint_S d\mathbf{S}_1 \cdot [(\nabla_1 - \nabla'_1) \hat{Z}_1 \gamma]. \quad (10)$$

If \hat{Z}_1 is the unit operator, equation (9) reduces to an integral form of the equation of continuity:

$$\frac{dM}{dt} = -\oint_S d\mathbf{S}_1 \cdot \hat{\mathbf{J}}_1 \gamma(\mathbf{x}_1 | \mathbf{x}'_1), \quad (11)$$

where we have defined a flux density operator

$$\hat{\mathbf{J}}_1 \equiv -\frac{i\hbar}{2m} (\nabla_1 - \nabla'_1). \quad (12)$$

Note that $\hat{\mathbf{J}}_1$ acts on primed as well as unprimed coordinates. The right-hand side of

equation (11) represents (the negative of) the total flux of electrons out through the closed surface S . Equation (9) may now be written

$$\frac{dM}{dt} = -\oint_S d\mathbf{S}_1 \cdot \hat{\mathbf{J}}_1 \hat{Z}_1 \gamma + \frac{i\hbar}{2m} \int_{\Omega} dv_1 [\hat{Z}_1, \Delta_1] \gamma + \frac{N}{i\hbar} \int_{\Omega} dv_1 \int_{\infty}' dv \hat{Z}_1 (V - V') \bar{\Psi}' \Psi. \quad (13)$$

This is, in fact, an equation of continuity of the observable corresponding to \hat{Z}_1 . When operating on $\hat{Z}_1 \gamma$, the operator $\hat{\mathbf{J}}_1$ yields the probability density of the flux density (flux per unit area) of the observable.

3. The generalized virial equation

To derive the virial equation from equation (13), \hat{Z}_1 is defined as the scalar product of the position vector and the linear momentum operator $\hat{\mathbf{p}}_1$:

$$\hat{Z}_1 \equiv \mathbf{x}_1 \cdot \hat{\mathbf{p}}_1 \equiv -i\hbar \mathbf{x}_1 \cdot \nabla_1. \quad (14)$$

This is a non-Hermitian operator; strictly we should use the operator

$$\hat{Z}_H \equiv \frac{1}{2}(\mathbf{x}_1 \cdot \hat{\mathbf{p}}_1 + \hat{\mathbf{p}}_1 \cdot \mathbf{x}_1) \equiv \hat{Z}_1 - \frac{3}{2}i\hbar, \quad (15)$$

but this operator yields the same final result as \hat{Z}_1 . (The constant operator $-\frac{3}{2}i\hbar$, inserted into equation (13), leads to the equation of continuity (11), the time average of which vanishes.) The commutator in equation (13) now is

$$[\hat{Z}_1, \Delta_1] \gamma = -i\hbar [\mathbf{x}_1 \cdot \nabla_1, \Delta_1] \gamma = 2i\hbar \Delta_1 \gamma. \quad (16)$$

The last integrand of equation (13) is

$$\begin{aligned} \hat{Z}_1 (V - V') \bar{\Psi}' \Psi &= -i\hbar \mathbf{x}_1 \cdot \nabla_1 (V - V') \bar{\Psi}' \Psi \\ &= -i\hbar \bar{\Psi}' (\Psi \mathbf{x}_1 \cdot \nabla_1 V + V \mathbf{x}_1 \cdot \nabla_1 \Psi - V' \mathbf{x}_1 \cdot \nabla_1 \Psi). \end{aligned} \quad (17)$$

When the primes are dropped prior to the integration, the two last terms of equation (17) are eliminated. Thus equation (13) can be written

$$\frac{dM}{dt} = -\oint_S d\mathbf{S}_1 \cdot (\hat{\mathbf{J}}_1 \mathbf{x}_1 \cdot \hat{\mathbf{p}}_1 \gamma) - 2 \int_{\Omega} dv_1 \frac{\hbar^2}{2m} \Delta_1 \gamma - N \int_{\Omega} dv_1 \int_{\infty}' dv \bar{\Psi} \Psi \mathbf{x}_1 \cdot \nabla_1 V. \quad (18)$$

The second term is recognized as twice the expectation value $\langle T \rangle$ of the kinetic energy, while the last term is the expectation value $Z_P = -\sum_i \langle \mathbf{x}_i \cdot \nabla_i V \rangle$ of the petit virial. The first term is the quantum *surface flux virial*

$$Z_S = -\oint_S d\mathbf{S} \cdot (\hat{\mathbf{J}} \mathbf{x} \cdot \hat{\mathbf{p}} \gamma(\mathbf{x}|\mathbf{x}')). \quad (19)$$

For convenience, we have dropped the index 1.

The time average of equation (18) obtains the form of a *grand virial equation*:

$$(2\langle T \rangle + Z_P + Z_S)_{\text{time average}} = 0, \quad (20)$$

since the time average of dM/dt must vanish if M is uniformly continuous and limited for all values of t . In the appendix, the petit virial Z_P is expressed in terms of density functions.

4. An alternative form of the surface flux virial

Note that the integrand of equation (19) describes the *flux of a virial* rather than the *virial of a flux* as in the classical Z_S of equation (3). If equation (19) is to be expressed analogously to the classical case, \hat{J} must act on $\hat{p}\gamma$ rather than on $\mathbf{x} \cdot \hat{p}\gamma$. It is easily verified that

$$\hat{J}(\mathbf{x} \cdot \hat{p})\gamma = \mathbf{x} \cdot (\hat{J}\hat{p})\gamma - \frac{i\hbar}{2m}\hat{p}\gamma, \quad (21)$$

where the dot product on the right-hand side now represents matrix multiplication, and

$$(\hat{J}\hat{p})\gamma \equiv \begin{pmatrix} \hat{J}_x\hat{p}_x & \hat{J}_y\hat{p}_x & \hat{J}_z\hat{p}_x \\ \hat{J}_x\hat{p}_y & \hat{J}_y\hat{p}_y & \hat{J}_z\hat{p}_y \\ \hat{J}_x\hat{p}_z & \hat{J}_y\hat{p}_z & \hat{J}_z\hat{p}_z \end{pmatrix} \gamma \quad (22)$$

is a *momentum flux tensor*. Substitution of equation (21) into equation (19) yields

$$Z_S = -\oint_S d\mathbf{S} \cdot [\mathbf{x} \cdot (\hat{J}\hat{p})\gamma] + \frac{i\hbar}{2m} \oint_S d\mathbf{S} \cdot \hat{p}\gamma. \quad (23)$$

The first integral is here expressed as a virial of a momentum flux (analogously to the classical case). The appearance of the last term is a consequence of the use of smeared-out wavefunctions, and lacks an analogy in the classical point-particle case. The last integral is proportional to the (transverse) momentum density, integrated all over the surface S . This integral will vanish unless the particles are accelerated through the observed volume Ω by an external field.

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Appendix. Equation of motion of the reduced density matrix of the first order

In the following derivation it is of crucial importance to observe the difference between two types of ‘fragmental’ or ‘regional’ average values:

$$M = \sum_i \int_{\Omega} dv_i \int'_{\infty} dv \bar{\Psi} \hat{Z}_i \Psi \quad (A.1)$$

and

$$R = \int_{\Omega} dv_1 \int'_{\infty} dv \bar{\Psi} \sum_i \hat{Z}_i \Psi. \quad (A.2)$$

As pointed out by Srebrenik and Bader (1974), all electrons are treated in an equivalent manner in the first type of average (M), while this is not the case in the second type (R).

M may be expressed as

$$M = \int_{\Omega} dv_1 \hat{Z}_1 \gamma^{(1)}(1|1'). \quad (\text{A.3})$$

The relationship between M and R is then given by

$$R = \frac{1}{N} M + \frac{2}{N} \int_{\Omega} dv_1 \int_{\infty} dv_2 \hat{Z}_2 \gamma^{(2)}(1, 2|1', 2'). \quad (\text{A.4})$$

(The definition of $\gamma^{(k)}$ includes the factor $\binom{N}{k}$.) Since the volume Ω may be arbitrarily chosen, we may neglect the integration $\int_{\Omega} dv_1$ in equation (A.4), and we obtain

$$\int_{\infty}' dv \bar{\Psi}' \sum_i \hat{Z}_i \Psi = \frac{1}{N} \hat{Z}_1 \gamma^{(1)}(1|1') + \frac{2}{N} \int_{\infty} dv_2 \hat{Z}_2 \gamma^{(2)}(1, 2|1', 2'). \quad (\text{A.5})$$

Analogously, for symmetric two-electron operators \hat{Z}_{ij} , we obtain

$$\begin{aligned} \frac{1}{2} \int_{\infty}' dv \bar{\Psi}' \sum_{i,j} \hat{Z}_{ij} \Psi &= \frac{1}{N} \int_{\infty} dv_2 \hat{Z}_{12} \gamma^{(2)}(1, 2|1', 2') \\ &+ \frac{3}{N} \int_{\infty} dv_2 \int_{\infty} dv_3 \hat{Z}_{23} \gamma^{(3)}(1, 2, 3|1', 2', 3') \end{aligned} \quad (\text{A.6})$$

where $\bar{\Psi}' \equiv \bar{\Psi}(1', 2, 3, \dots, N)$. Equations (A.5) and (A.6) give the type of averages that appear in the derivation of the equation of motion of $\gamma^{(1)}$ from the time dependent Schrödinger equation:

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}. \quad (\text{A.7})$$

The complex conjugate of (A.7) may be expressed as

$$\hat{H}''\bar{\Psi}'' = -i\hbar \frac{\partial \bar{\Psi}''}{\partial t} \quad (\text{A.8})$$

where $\bar{\Psi}'' \equiv \bar{\Psi}(1', 2', 3, \dots, N)$. Analogously, the two first coordinates of \hat{H}'' are primed. If (A.7) is multiplied by $\bar{\Psi}''$ and (A.8) by $-\Psi$, and the results are summed up, one obtains

$$\bar{\Psi}'' \hat{H}\Psi - \Psi \hat{H}''\bar{\Psi}'' = i\hbar \frac{\partial}{\partial t} (\bar{\Psi}''\Psi). \quad (\text{A.9})$$

The Hamiltonian operator is

$$\hat{H} = -\kappa \sum_i \Delta_i + \sum_i h(i) + \frac{1}{2} \sum_{i,j} g(i, j) \quad (\text{A.10})$$

where $\kappa = \hbar^2/2m$ and h and g are one- and two-electron potentials, respectively. Insert \hat{H} (and the analogous expression for \hat{H}'') into equation (A.9) and perform the integration

$$\int_{\infty}' dv \equiv \int_{\infty} dv_2 \int_{\infty}'' dv \equiv \int_{\infty} dv_2 \int_{\infty} dv_3 \int_{\infty}''' dv.$$

Utilizing equations (A.5) and (A.6) and the fact that

$$\bar{\gamma}^{(k)}(1', 2', \dots, k'|1, 2, \dots, k) = \gamma^{(k)}(1, 2, \dots, k|1', 2', \dots, k'),$$

one obtains

$$\begin{aligned}
 & -\frac{\kappa}{N}(\Delta_1 - \Delta'_1)\gamma^{(1)}(1|1') - \frac{2\kappa}{N} \int_{\infty} dv_2(\Delta_2 - \Delta'_2)\gamma^{(2)}(1, 2|1', 2') \\
 & \quad + \frac{1}{N}(h(1) - h(1'))\gamma^{(1)}(1|1') + \frac{2}{N} \int_{\infty} dv_2(h(2) - h(2'))\gamma^{(2)}(1, 2|1', 2') \\
 & \quad + \frac{1}{N} \int_{\infty} dv_2(g(1, 2) - g(1', 2'))\gamma^{(2)}(1, 2|1', 2') \\
 & \quad + \frac{3}{N} \int_{\infty} dv_2 \int_{\infty} dv_3(g(2, 3) - g(2', 3'))\gamma^{(3)}(1, 2, 3|1', 2', 3') \\
 & = \frac{i\hbar}{N} \frac{\partial}{\partial t} \gamma^{(1)}(1|1'). \tag{A.11}
 \end{aligned}$$

The first integral in equation (A.11) can be transformed into a surface integral by means of Green's first identity:

$$\int_{\infty} dv_2(\Delta_2 - \Delta'_2)\gamma^{(2)} \rightarrow \oint_{\infty} d\mathbf{S}_2 \cdot (\nabla_2 - \nabla'_2)\gamma^{(2)} \tag{A.12}$$

which reduces to zero for a system with vanishing Ψ and derivatives of Ψ at infinity. The second and the last integrals of equation (A.11) vanish when the primes on coordinates 2 and 3 are dropped prior to the integration. Thus, equation (A.11) is reduced to

$$\begin{aligned}
 & -\kappa(\Delta_1 - \Delta'_1)\gamma^{(1)}(1|1') + (h(1) - h(1'))\gamma^{(1)}(1|1') \\
 & \quad + \int_{\infty} dv_2(g(1, 2) - g(1', 2))\gamma^{(2)}(1, 2|1', 2) = i\hbar \frac{\partial}{\partial t} \gamma^{(1)}(1|1') \tag{A.13}
 \end{aligned}$$

which is an *equation of motion of $\gamma^{(1)}$* . The somewhat simpler equation of motion used in the article (equation (7)), is easily derived in an analogous manner.

In the virial equation (18) of § 3, the petit virial Z_P may be expressed in terms of density matrices as follows:

$$\begin{aligned}
 Z_P & = -N \int_{\Omega} dv_1 \int_{\infty}' dv \bar{\Psi} \Psi \mathbf{x}_1 \cdot \nabla_1 V \\
 & = - \int_{\Omega} dv_1(\mathbf{x}_1 \cdot \nabla_1 h(1))\gamma^{(1)}(1|1) - \int_{\Omega} dv_1 \int_{\infty} dv_2(\mathbf{x}_1 \cdot \nabla_1 g(1, 2))\gamma^{(2)}(1, 2|1, 2). \tag{A.14}
 \end{aligned}$$

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