Virial Theorem for Many-Electron Dirac Systems*

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The virial theorem is derived for a system of N relativistic electrons interacting with each other via electrostatic forces and subject to arbitrary external electromagnetic fields. The results are presented in a form that is useful in perturbation calculations and investigations of nonisotropic systems. The equation of state for a system of N electrons confined to a box is discussed on the basis of the virial theorem.

I. INTRODUCTION

THE standard quantum mechanical versions of the virial theorem refer to a single nonrelativistic or relativistic particle or to a system of N nonrelativistic particles.[1,2] In this note, we show that the single-particle Dirac virial theorem can be generalized to the N-particle case in a manner analogous to the nonrelativistic generalization; the results apply to a system of N relativistic electrons interacting via electrostatic forces and subject to arbitrary external electromagnetic fields. The complete identity, of which the virial theorem is a special case, applies to off-diagonal matrix elements and is a tensor, not a scalar, relation. This general form of the virial theorem can be applied in perturbation calculations and in investigations of nonisotropic systems[3]; the relations may be useful in discussing high-temperature plasmas. We employ the virial theorem to describe the equation of state for a system of N relativistic electrons confined to a box, and obtain results analogous to those found in the nonrelativistic case.

II. VIRIAL THEOREM

We consider a system of N electrons whose behavior is governed by the following Hamiltonian[4]:

$$H=\sum_{i=1}^{N}\{\boldsymbol{\alpha}(i)\cdot\boldsymbol{\pi}(i)+\beta(i)+V(i)\}+\sum_{i<j}I(i,j), \quad (1)$$

where

$$\boldsymbol{\pi}(i)=\mathbf{p}(i)+e\mathbf{A}(i).$$

The quantities $V(i)$ and $\mathbf{A}(i)$ are the external scalar and vector potentials evaluated at the position of the ith particle, and $I(i,j)$ represents the interaction between the electrons. For many cases of interest,

$$V(i)=-Ze^2/r_i, \quad (2)$$

and

$$I(i,j)=e^2/r_{ij}, \quad (3)$$

but the particular form of V and I will not be important in what follows; we shall only make use of the fact that they depend solely on the coordinates of the particles. The largest interelectron interaction that is omitted in the Hamiltonian of Eq. (1) corresponds to the exchange of a single virtual photon; this omitted term is of order v^2/c^2 times the electrostatic interaction and hence of order α^2Z times the leading terms of (1) for bound atomic electrons.[5,6] In general, the relativistic effects included in Eq. (1) are of order $(v^4/c^4)mc^2$ and the omitted one-photon exchange is of order $(v^2/c^2)\langle e^2/r_{12}\rangle$. The omitted term is small for low-density plasmas. We neglect effects associated with the creation of real photons or electrons; these effects are most important at high densities.

The generalized virial theorem is obtained by considering[7]

$$\langle a|\,(d/dt)M_{\gamma\beta}|\,b\rangle, \quad (4)$$

where

$$M_{\gamma\beta}=\sum_{j=1}^{N}x_\gamma(j)\pi_\beta(j), \quad (5)$$

and N is the number of electrons in the system. We write,[1,2]

$$\langle a|\,(d/dt)M_{\gamma\beta}|\,b\rangle=i\langle a|\,[H,M_{\gamma\beta}]\,|\,b\rangle$$
$$=i(E_a-E_b)\langle a|\,M_{\gamma\beta}|\,b\rangle+S_{\gamma\beta}, \quad (6)$$

where $S_{\gamma\beta}$ is a boundary term that arises because H is not Hermitian, in the usual sense, for continuum states. Evaluating the commutator and performing the appropriate partial integration in (6), we find

$$2\langle a|\,T_{\gamma\beta}|\,b\rangle=-\langle a|\sum_{j=1}^{N}x_\gamma(j)F_\beta(j)\,|\,b\rangle+S_{\gamma\beta}, \quad (7)$$

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[1] The virial theorem in quantum mechanics has been reviewed by R. M. Schectman and R. H. Good, Am. J. Phys. **25**, 219 (1957). A complete list of references is contained in this article.

[2] The single-particle Dirac virial theorem is discussed in detail in M. E. Rose, *Relativistic Electron Theory* (John Wiley & Sons, Inc., New York, 1961), p. 132.

[3] For a discussion of the applications of the classical tensor form of the virial theorem to nonisotropic systems, see E. N. Parker, Phys. Rev. **96**, 1686 (1954).

[4] We use units in which $\hbar=m=c=1$.

[5] J. N. Bahcall and D. Layzer, Ann. Phys. (to be published). For bound atomic electrons, the relativistic effects retained in Eq. (1) are of order α^4Z^4; the omitted one-photon exchange interaction (the Breit interaction) is of order α^4Z^3. The neglect of the α^4Z^3 term seriously limits the usefulness of the virial theorem for relativistic atomic systems, but appears unavoidable since the Breit interaction, which arises in perturbation theory, cannot be used in Eq. (6).

[6] The omitted interaction for free electrons is the well-known Møller correction to Coulomb scattering.

[7] $M_{\gamma\beta}$ is the generalized time derivative of the moment of inertia.

where

$$T_{\gamma\beta}=\sum_{j=1}^{N}\alpha_\gamma(j)\pi_\beta(j), \tag{8}$$

$$F_\beta(j)=-\nabla_\beta(j)[V(\mathbf{r}_j)+\textstyle\sum_k I(\mathbf{r}_{jk})] -e[\boldsymbol{\alpha}(j)\times\mathbf{H}(j)]_\beta-i(E_a-E_b)\pi_\beta(j), \tag{9}$$

and

$$S_{\gamma\beta}=i\sum_{i,j}\int d\tau\ \mathbf{p}(i)\cdot\{\psi_a^\dagger\boldsymbol{\alpha}(i)x_\gamma(j)\pi_\beta(j)\psi_b\}, \tag{10}$$

where

$$d\tau=\prod_{i=1}^{N}d\tau_i.$$

The sum of the diagonal components of T is the generalized kinetic energy; F is the Lorentz force; and S is the surface term. Since Eq. (7) has been derived for arbitrary matrix elements, it can be used in perturbation calculations in which off-diagonal matrix elements must be considered. The tensor form of (7) enables one to apply the results to nonisotropic systems.

The meaning of the surface term S can be found by a procedure due to Cottrell and Paterson.[8] We consider a system composed of N electrons confined to a volume $V=L^3$ and assume that ψ_a and ψ_b are zero whenever any of the electrons is on the bounding surface. One can show that

$$\sum_\gamma S_{\gamma\gamma}=L(E_a-E_b)\left[\int d\tau\ \psi_a^\dagger\frac{\partial}{\partial L}\psi_b\right]-L\frac{\partial E_b}{\partial L}\delta_{a,b}. \tag{11}$$

Thus, for diagonal matrix elements

$$\textstyle\sum_\gamma S_{\gamma\gamma}=-L(\partial E/\partial L) =3PV, \tag{12}$$

where P is the pressure exerted by the electrons on the walls of the container.[9] Hence, Eq. (7) can be specialized to

$$PV=\tfrac{2}{3}\langle a|\textstyle\sum_\gamma T_{\gamma\gamma}|a\rangle+\tfrac{1}{3}\langle a|\sum_j\mathbf{x}(j)\cdot\mathbf{F}(j)|b\rangle. \tag{13}$$

Equations of this form have been used in discussing equations of state[10] and the equivalence of kinetic and thermodynamic pressure.[11]

Formulas (11) and (13) have been derived by requiring that ψ be zero whenever any of the electron coordinates is on the surface. However, for free Dirac particles, one cannot form a linear superposition of the four periodic positive-energy solutions, two each corresponding to plus and minus $\mathbf{p}$, that vanishes on the surface of quantization.[12] Thus, it is of interest to evaluate S directly with periodic momentum eigenfunctions. Ignoring all interactions, we find

$$S_{\gamma\beta}=\sum_k\frac{p_\gamma(k)p_\beta(k)}{E(k)}. \tag{14}$$

If there is no macroscopic motion of the gas, Eq. (14) yields

$$\textstyle\sum_\gamma S_{\gamma\gamma}=\sum\mathbf{p}(k)\cdot\mathbf{v}(k) =3PV, \tag{15}$$

which is identical with the previously obtained result, (12).

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[8] T. L. Cottrell and S. Paterson, Phil. Mag. **42**, 391 (1951).
[9] We neglect radiation pressure.
[10] J. C. Slater, J. Chem. Phys. **1**, 687 (1933); R. B. Lindsay, *Introduction to Physical Statistics* (John Wiley & Sons, Inc., New York, 1941), Chap. V.
[11] J. de Boer, Physica **15**, 843 (1949); R. J. Riddell, Jr., and G. E. Uhlenbeck, J. Chem. Phys. **18**, 1066 (1950).
[12] The combination $\psi(+p)-\psi(-p)$ does not vanish on the surface and $\psi(+p)-\beta\psi(-p)$ is not an energy eigenfunction.