Pramāṇa, Vol. 23, No. 2, August 1984, pp. L275–L278. © Printed in India.

Conditions for the relativistic virial theorem for one electron

SAMBHU N DATTA
Department of Chemistry, Indian Institute of Technology, Bombay 400 076, India

MS received 7 May 1984

Abstract. Conditions for the usual form of one-electron relativistic virial theorem to be satisfied are derived and illustrated. These can be applied to generate quality basic spinors for solving a one-electron Dirac equation.

Keywords. Relativistic virial theorem; uniform scale variation; basic spinor; one electron Dirac equation.

PACS No. 03·65–W; 31·10+z; 31·15+q

Recent years have seen a surge in investigation of relativistic effects in atoms and molecules and it has become increasingly important to establish relativistic virial relations for such systems. This can be done in three distinct stages. The first step involves specifying virial relations for an *arbitrary* spinor which is an approximate solution of the one-electron Dirac Hamiltonian. Next, one needs to evaluate such relations for interacting fermions, but the derivation is not expected to be as trivial as it may seem in the nonrelativistic case; complications are expected to arise from the *proper* choice of a many-body Dirac Hamiltonian and from the proper maintenance of the relationship between the upper and lower components of spinors used in defining a many-electron state. Finally one must investigate implications of the renormalization procedure. This work explores the conditions when relativistic virial theorem will be obeyed for a single electron.

Dirac Hamiltonian H_D and an arbitrary spinor ψ_D are written as

$$H_D = c^2\beta + c\alpha\cdot p + V \equiv c^2\beta + T + V = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \tag{1}$$

and $$\psi_D = \begin{pmatrix} \mu \\ \nu \end{pmatrix},$$

where α and β are the usual Dirac matrices, V the scalar potential and $T = c\alpha\cdot p$ is the kinetic energy term; μ and ν are respectively upper and lower components of the four-component spinor ψ_D, and H_{11}, H_{12}, H_{21}, and H_{22} are all 2×2 matrix operators. Let the scalar potential be a homogeneous function of degree ρ in coordinates. The usual variation of scale to extremize the energy expectation value E (Fock 1978) results in the relativistic virial theorem for a single electron, $\langle T\rangle = \rho\langle V\rangle$. For coulomb interactions $\rho = -1$ so that $E = c^2\langle\beta\rangle$. An identical result can be obtained for eigenstates (Rose and Welton 1952; Schiff 1968). March (1953) improved the Fock virial theorem for spinors that do not vanish at the boundary. Rosicky and Mark (1975) considered

maintenance of intercomponent relationships such that E is minimized, derived a pseudoeigenvalue equation for the upper component μ and achieved a generalized virial relation for spinors with arbitrary boundary conditions. None of these derivations uses a spinor which is arbitrary enough. In the usual derivation it is implicitly assumed that the scaling in upper and lower components has been uniform,

$$\mu(x) \to \lambda^{3/2}\, \mu(\lambda x),$$
$$\nu(x) \to \lambda^{3/2}\, \nu(\lambda x),$$
$$\text{such that} \quad \psi(x) \to \lambda^{3/2}\, \psi(\lambda x), \tag{2}$$

requiring a similar coordinate dependence for both the components. The derivation of Rosicky and Mark (1975) instead employs a specific relationship between these two components. This work imposes no such restriction, to start with, on the spinors but adheres to the standard boundary condition, *i.e.*, the wavefunction vanishes at the boundary (for atomic and molecular systems).

Relativistic virial theorem for one electron

Since H_D contains an odd operator it is imperative that an operator $\hat{\Omega}$ should be considered to relate ν with μ,

$$|\nu) = \hat{\Omega}\,|\mu), \tag{3}$$

whereby Dirac equation is rewritten as

$$(\mu, [(H_{11} - E) + H_{12}\hat{\Omega} + \hat{\Omega}^{+} H_{21} + \hat{\Omega}^{+} (H_{22} - E)\hat{\Omega}]\mu) = 0. \tag{4}$$

A stationary E is obtained for $\hat{\Omega} = (E - H_{22})^{-1} H_{21}$ which is the starting point of constrained-component variation (Datta and Jagannathan 1984) and the Rosicky-Mark (1975) virial theorem.

If one directly considers a scaling $\mu(x) \to \lambda^{3/2}\mu(\lambda x)$ in (4) one obtains, after some rearrangement,

$$(\mu, [(c^2 + \lambda^{-\rho} e\Phi - E_\lambda) + \lambda H_{12}\hat{\Omega}_\lambda + \lambda \hat{\Omega}_\lambda^{+} H_{21} + \hat{\Omega}_\lambda^{+} (-c^2 + \lambda^{-\rho} e\Phi - E_\lambda)\hat{\Omega}_\lambda]\mu) = 0, \tag{4a}$$

such that a variation of scale to make E stationary yields

$$(\mu, [H_{12}\hat{\Omega}_\lambda + \hat{\Omega}_\lambda^{+} H_{21}]\mu) - \rho\lambda^{-\rho-1} (\mu, [e\Phi + \hat{\Omega}_\lambda^{+} e\Phi\hat{\Omega}_\lambda]\mu)$$
$$+ (\mu, [\{\lambda H_{12} - \hat{\Omega}_\lambda^{+} (E_\lambda + c^2 - \lambda^{-\rho} e\Phi)\} \left(\frac{\partial \hat{\Omega}_\lambda}{\partial \lambda}\right) + \text{h.c.}]\mu) = 0. \tag{4b}$$

But the result of this variation is to be considered at $\lambda = 1$ (Fock 1978), *i.e.*,

$$(\mu, [H_{12}\hat{\Omega} + \hat{\Omega}^{+} H_{21}]\mu) - \rho(\mu, [e\Phi + \hat{\Omega}^{+} e\Phi\hat{\Omega}]\mu)$$
$$+ (\mu, [\{H_{12} - \hat{\Omega}_\lambda^{+} (E - H_{22})\} (\partial\hat{\Omega}/\partial\lambda)_{\lambda=1} + \text{h.c.}]\mu) = 0. \tag{4c}$$

Finally one makes the identification that

$$\langle T \rangle_\psi = (\mu, [H_{12}\hat{\Omega} + \hat{\Omega}^{+} H_{21}]\mu)\, (\mu, [1 + \hat{\Omega}^{+}\Omega]\mu)^{-1}$$

and

$$\langle V \rangle_\psi = (\mu, [e\Phi + \hat{\Omega}^{+} e\Phi\hat{\Omega}]\mu)\, (\mu, [1 + \hat{\Omega}^{+}\hat{\Omega}]\mu)^{-1} \tag{4d}$$

so that the exact one-electron relativistic virial theorem with the standard boundary condition is given by

$$\langle T\rangle_\psi - \rho\langle V\rangle_\psi + (\mu,[\{H_{12}-\hat{\Omega}^+(E-H_{22})\}(\partial\hat{\Omega}/\partial\lambda)_{\lambda=1}+\text{h.c.}]\mu) (\mu,[1+\hat{\Omega}^+\hat{\Omega}]\mu)^{-1} = 0 \tag{5}$$

which differs from its usual form by virtue of the third term on the left side of (5).

Hence the usual relativistic virial theorem will be satisfied only when $\hat{\Omega}$ is independent of coordinates, or $\hat{\Omega} = (E-H_{22})^{-1}H_{21}$ or $(\mu,(H_{12}-\hat{\Omega}^+(E-H_{22})(\partial\hat{\Omega}/\partial\lambda)_{\lambda=1}\mu)$ is purely imaginary. For other choices of $\hat{\Omega}$, μ and ν do not exhibit a parallel scaling.

If $\hat{\Omega}$ is independent of coordinates, relativistic virial theorem is read as $\langle V\rangle_\psi = 0$ which indicates that for a nonvanishing external potential no nontrivial solution of Dirac equation can be obtained with a E stationary with variation of scale, and with proportional upper and lower components (in the sense of matrix products). If V is the null matrix, μ and ν may have any well-behaved functional appearance and will satisfy $\hat{\Omega} = (E-H_{22})^{-1}H_{21}$ (as is also required from direct contraction of Dirac equation) if they are plane waves. That is, "free" particle solutions correspond to proportional upper and lower components whereby a parallel scaling is achieved for both.

The second possibility, $\hat{\Omega} = (E-H_{22})^{-1}H_{21}$, indicates another reason why a constrained-component variation is preferred over a general variational procedure in finding the likely solution of Dirac equation (Datta and Jagannathan 1984).

The third condition, $(\mu,[H_{12}-\hat{\Omega}^+(E-H_{22})](\partial\hat{\Omega}/\partial\lambda)_{\lambda=1}\mu)$, which is purely imaginary is more involved and will be illustrated elsewhere.

Illustrations

Virial relation is important in that it often serves as a criterion for obtaining a good solution of a wave equation; it also serves as a check on the quality of wavefunctions resulting from a SCF analysis. An immediate application of relativistic virial theorem will be in deciding the nature of basic spinors to be used in a Dirac-Fock calculation (Datta and Ewig 1982). Thus a rather easy short-cut to generate an approximate inter-component relationship, $\hat{\Omega} = (2c^2)^{-1}H_{21}$, that has been used in several recent Dirac-Fock calculations (Ishikawa *et al* 1983; Lee and McLean 1982) corresponds to a nonuniform scale variation for the spinor-components and one should not expect relativistic virial theorem to be satisfied in the conventional form.

The effort is of course considerably reduced if a choice of $\hat{\Omega}$ is indicated such that a parallel scaling is achieved for both μ and ν. This situation is being illustrated for a hydrogen-like Hamiltonian with the nuclear charge Z' and a model upper component.

$$\mu = N_\psi R_r(r) X_{-nm} \tag{6}$$

where $R_n(r) = N_n r^{n-1}\exp(-\varepsilon r)$ and N's are appropriate normalization constants. For $n = 1$ the following choice of $\hat{\Omega}$ is made.

$$\hat{\Omega} = ((|\kappa|-\gamma)/(|\kappa|+\gamma))^{1/2}\varepsilon^{-1}\tau\cdot p \tag{7}$$

where τ is the Pauli spin matrix and X is a two-component spinor involving angular

coordinates such that $c^2\langle\beta\rangle$ is given by its correct form, $\gamma c^2/|\kappa|$. In (7) γ is related to $|\kappa|$, $\gamma = (|\kappa|^2 - Z^2/c^2)^{1/2}$, but $|\kappa|$ is yet to be determined. This spinor gives

$$E = \frac{\gamma}{|\kappa|}c^2 + \varepsilon Z\left(\frac{1}{|\kappa|} - \frac{Z'}{Z}\right) \tag{8}$$

and hence for any exponent ε, relativistic virial theorem is always satisfied if $|\kappa| = Z/Z'$. For $|\kappa| = 1$, E equals energy of $1s_{\pm 1/2}$ spinor of the hydrogen-like atom ($Z' = Z$) whereas $|\kappa| = 1/2$ gives the energy of the $1s_{\pm 1/2}$ spinor of the He^+-like ion ($Z' = 2Z$); these trends are important in the consideration of separated and united atom limits for the H_2^+-type molecular ion. A unique value of the scaling parameter ε is not generated unless a $\hat{\Omega}$-variation is performed to make E stationary. This is achieved, presently, by considering $\partial E/\partial|\kappa| = 0$ which yields the exponent $\varepsilon = Z/\gamma = |\kappa|(Z'/\gamma)$. It is remarkable that the same value of the exponent is obtained by Dyall *et al* (1984) from a consideration of the matrix representation of operator products.

This work was carried out with the financial support from CSIR. The author thanks Dr Ishikawa for sending him reprints and preprints of their recent manuscripts.

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