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# Relativistic virial theorem for atoms

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**Abstract.** A relativistic virial theorem is derived for atoms in a general manner. The virial ratio consists of the usual $V/T$ term and a correction term $W/T$, where $T$, $V$, and $W$ are the kinetic energy, the potential energy, and correction terms, respectively. Explicit forms of $W$ are presented for four specific nuclear potential models. Numerical calculations for a uniform nuclear charge model show that the magnitude of the correction term $W/T$ increases with increasing atomic numbers and that it modifies the ratio $V/T$ considerably for atoms with large atomic numbers in particular.

**Key words:** Virial theorem – Relativistic – Atom – Nucleus model

## 1 Introduction

In nonrelativistic atomic and molecular calculations, atomic nuclei are usually treated as point charges (PCs), while in relativistic calculations they are often assumed to have finite sizes and such nucleus models are adopted as a uniformly charged sphere (UCS), a Gaussian charge distribution (GCD), and a Fermi charge distribution (FCD) [1, 2].

The virial theorem (VT) for atoms in the PC nuclear potentials is well known; for nonrelativistic atoms it is presented in many textbooks (e.g., Ref. [3]) and review articles (e.g., Ref. [4]) and for relativistic atoms it was derived by Kim [5] and Mohanty and Clementi [6]. Although the VT for a Dirac one-particle system in a general potential was reported by Rose and Welton [7] about a half century ago, the relativistic VT for many-electron atoms in general nuclear potentials is not known.

In this article, we derive the relativistic VT for many-electron atoms in a general nuclear potential and apply it to the specific nuclear potentials appearing in the previously mentioned four kinds of nucleus models, PC, UCS, GCD, and FCD. We also present some numerical results for the UCS model using the Dirac–Fock–Roothaan (DFR) method [5]. Throughout this report, Hartree atomic units are used.

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## 2 VT in a general nuclear potential

For an $n$-electron atom, we consider an arbitrary normalized four-component wave function,

$$\phi(1) = \psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) \ , \tag{1}$$

and its normalized scaled function with respect to the position coordinates, $\mathbf{r}_i$ ($i = 1, \ldots, n$), of electrons,

$$\phi(\lambda) = \lambda^{3n/2}\psi(\lambda\mathbf{r}_1, \lambda\mathbf{r}_2, \ldots, \lambda\mathbf{r}_n) \ . \tag{2}$$

The energy expectation value over the scaled function is

$$E(\lambda) = \langle\phi(\lambda)\big|\hat{H}\big|\phi(\lambda)\rangle \ , \tag{3}$$

where the Dirac–Coulomb–Breit Hamiltonian $\hat{H}$ [1, 5] may be conveniently divided into kinetic energy, $\hat{T}$, mass energy, $\hat{M}$, and total potential energy, $\hat{V}$, components:

$$\hat{H} = \hat{T} + \hat{M} + \hat{V} \tag{4}$$

in which

$$\hat{T} = \sum_{i=1}^{n} c\alpha_i\mathbf{p}_i \ , \tag{5}$$

$$\hat{M} = \sum_{i=1}^{n} c^2\beta_i \ , \tag{6}$$

$$\hat{V} = \sum_{i=1}^{n} v(\mathbf{r}_i) + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} g(\mathbf{r}_{ij}) \ . \tag{7}$$

In Eqs. (5) and (6), $c$ is the speed of light, $\alpha_i$ and $\beta_i$ are Dirac matrices [5], and $\mathbf{p}_i = -\mathrm{i}\nabla_i$ is momentum operator for electron $i$. In Eq. (7), $v(\mathbf{r}_i)$ is the nuclear attraction potential for electron $i$ and $g(\mathbf{r}_{ij})$ is the Coulomb–Breit interaction:

$$g(\mathbf{r}_{ij}) = \frac{1}{\mathbf{r}_{ij}} - \frac{1}{2}\left[\frac{\alpha_i \cdot \alpha_j}{\mathbf{r}_{ij}} + \frac{(\alpha_i \cdot \mathbf{r}_{ij})(\alpha_j \cdot \mathbf{r}_{ij})}{\mathbf{r}_{ij}^3}\right] \ , \tag{8}$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ and $\mathbf{r}_{ij} = |\mathbf{r}_{ij}|$ are the relative position vector and distance between two electrons $i$ and $j$.

If we put $\mathbf{r}_i' = \lambda \mathbf{r}_i$ $(i = 1, 2, \ldots, n)$, Eq. (3) is rewritten as

$$\begin{aligned} E(\lambda) = \int \mathrm{d}\mathbf{r}_1' \mathrm{d}\mathbf{r}_2' \ldots \mathrm{d}\mathbf{r}_n' \psi^\dagger(\mathbf{r}_1', \mathbf{r}_2', \ldots, \mathbf{r}_n') \\ \times \left[\lambda \sum_i c\alpha_i \mathbf{p}_i' + \sum_i c^2 \beta_i + \lambda \sum_{i<j} g(\mathbf{r}_{ij}')\right. \\ \left. + \sum_i v(r_{ij}'/\lambda)\right] \psi(\mathbf{r}_1', \mathbf{r}_2', \ldots, \mathbf{r}_n') \ . \end{aligned} \tag{9}$$

We regard the scale factor $\lambda$ as a variational parameter and determine its optimum value by requiring that

$$\begin{aligned} \frac{\partial E(\lambda)}{\partial \lambda} = \langle \phi(1) | \hat{T} | \phi(1) \rangle + \left\langle \phi(1) \left| \sum_{i<j} g(\mathbf{r}_{ij}) \right| \phi(1) \right\rangle \\ + \left\langle \phi(1) \left| \frac{\partial}{\partial \lambda} \sum_i v(\mathbf{r}_i/\lambda) \right| \phi(1) \right\rangle = 0 \ . \end{aligned} \tag{10}$$

The operator in the third term turns out to be

$$\frac{\partial}{\partial \lambda} v(\mathbf{r}/\lambda) = -\frac{1}{\lambda^2} \mathbf{r} \cdot \nabla'' v(\mathbf{r}'') \ , \tag{11}$$

where $\mathbf{r}'' = \mathbf{r}/\lambda$ and $\nabla''$ is the gradient operator with respect to the position vector $\mathbf{r}''$.

If the wave function $\phi(1)$ given by Eq. (1) is already optimum, we may put $\lambda = 1$ in Eqs. (10) and (11) and obtain a VT:

$$\begin{aligned} \langle \phi(1) | \hat{T} | \phi(1) \rangle + \left\langle \phi(1) \left| \sum_{i<j} g(\mathbf{r}_{ij}) \right| \phi(1) \right\rangle \\ - \left\langle \phi(1) \left| \sum_i \mathbf{r}_i \cdot \nabla v(\mathbf{r}_i) \right| \phi(1) \right\rangle = 0 \ . \end{aligned} \tag{12}$$

By adding the nuclear potential $\sum_i v(\mathbf{r}_i)$ to the second term and subtracting it from the third term, we have another form of the VT:

$$T + V + W = 0 \ , \tag{13}$$

where $T$ is the kinetic energy corresponding to the first term in Eq. (12), $V$ is the expectation value for the total potential-energy operator defined by Eq. (7), and $W$ is the expectation value,

$$W = \left\langle \phi(1) \left| \sum_i w(\mathbf{r}_i) \right| \phi(1) \right\rangle \ , \tag{14}$$

of an operator defined by

$$w(\mathbf{r}) = -\mathbf{r} \cdot \nabla v(\mathbf{r}) - v(\mathbf{r}) \ . \tag{15}$$

The VT given by Eq. (13) shows that the virial ratio consists of the familiar $V/T$ term and a correction term $W/T$.

Since the total energy, $E$, is expressed with the mass energy, $M = \langle M \rangle$, as

$$E = T + M + V \ , \tag{16}$$

we obtain an alternative form of the VT of Eq. (13) as

$$E - M + W = 0 \ . \tag{17}$$

For hydrogen-like atoms, the VT of Eq. (17) reduces to the VT for the Dirac one-particle system reported in Ref. [7]. We note that all the results in this section remain unaltered even if the Breit correction in Eq. (8) is not considered.

## 3 VT for specific nuclear potentials

The VTs of Eqs. (12), (13), and (17) take different forms for different nuclear potentials, $v(\mathbf{r})$. In this section, explicit expressions for the operator $w(\mathbf{r})$ defined by Eq. (15) are derived for four nuclear potentials often used in current relativistic atomic calculations. If we substitute these results into Eq. (14), we obtain the expectation values, $W$, appearing in the relativistic VTs.

### *3.1 PC nucleus*

The nuclear potential is written as

$$v(\mathbf{r}) = -Z/r \ , \tag{18}$$

where $Z$ is the nuclear charge and $r = |\mathbf{r}|$. Using Euler's theorem for homogeneous functions [8], we find

$$w(\mathbf{r}) = 0 \ . \tag{19}$$

Hence the $W$ term in the VTs is absent. This form of the VT is already known in the literature [5, 6].

### *3.2 UCS nucleus*

The UCS nuclear potential takes the form [1]

$$v(\mathbf{r}) = -\frac{Z}{2R}\left[3 - \left(\frac{r}{R}\right)^2\right]\Theta\left(\frac{R-r}{R}\right) - \frac{Z}{r}\Theta\left(\frac{r-R}{R}\right) \ , \tag{20}$$

where $R$ is the nuclear radius and $\Theta(x)$ is Heaviside step function. By putting this potential into Eq. (15) and noting that terms arising from the differentiation of the step functions cancel out in the integral of Eq. (14), we obtain

$$w(\mathbf{r}) = \frac{3Z}{2R}\left[1 - \left(\frac{r}{R}\right)^2\right]\Theta\left(\frac{R-r}{R}\right) \ , \tag{21}$$

which contributes only for the region $r < R$.

### 3.3 GCD and FCD nucleus models

In the GCD and FCD nucleus models, the nuclear potential is commonly written as [1, 2]

$$v(\mathbf{r}) = -Z \int \mathrm{d}\mathbf{s}\ \rho(s) \frac{1}{|\mathbf{r}-\mathbf{s}|}\ , \tag{22}$$

where $\rho(s)$ is a spherical nuclear charge density and the integration is performed over the whole space of the nuclear charge coordinate, $\mathbf{s}$. The explicit forms of $\rho(s)$ in the GCD and FCD models are

$$\rho(s) = (\alpha/\pi)^{3/2} \exp(-\alpha s^2)\ \text{(Gauss)}\ , \tag{23}$$

$$\rho(s) = \rho_0/\{1 + \exp[(s-a)/d]\}\ \text{(Fermi)}\ , \tag{24}$$

where $\alpha$, $\rho_0$, $a$, and $d$ are parameters [1, 2].

By putting Eq. (22) into Eq. (15), we obtain

$$w(\mathrm{r}) = Z \int \mathrm{d}\mathbf{s}\rho(s) \left[ \frac{\mathbf{r}\cdot(\mathbf{r}-\mathbf{s})}{|\mathbf{r}-\mathbf{s}|^3} + \frac{1}{|\mathbf{r}-\mathbf{s}|} \right]\ . \tag{25}$$

## 4 Numerical example

In order to see how the virial ratio $V/T$ is affected by the $W/T$ term, we performed DFR calculations [5] on various neutral atoms in their ground states. We adopted the UCS nucleus model, in which the nuclear radii, $R$, were taken from Visscher and Dyall [9]. We assumed the speed of light to be 137.0359895. As in a previous calculation [10], we adopted Gaussian-type functions (GTFs) as basis functions and neglected the Breit interaction term in the two-electron operator of Eq. (8).

For our purpose, it is necessary to compute atomic integrals of the $w$ operator (Eq. 21) over the GTFs, whose radial part is given by

$$R_{n\zeta}(r) = r^{n-1} \exp(-\zeta r^2)\ , \tag{26}$$

where $\zeta$ is exponent parameter (EP) and $n$ is a positive integer. If we are reminded that $w(\mathbf{r}) = w(r)$ for the UCS nucleus model, the integral is obtained as

$$\int_0^R \mathrm{d}r\ r^2 R_{n\zeta}(r) w(r) R_{n'\zeta'}(r) = (3Z/2)R^{2v}[F_v(\xi) - F_{v+1}(\xi)]\ , \tag{27}$$

where $R$ is the nuclear radius, $v = (n+n')/2$, $\xi = (\zeta+\zeta')R^2$, and

$$F_v(t) = \int_0^1 \mathrm{d}u u^{2v} \exp(-tu^2) \tag{28}$$

is the reduced incomplete Gamma function.

Some results of our numerical calculations are summarized in Table 1. For each atom, the first line shows the result using nonrelativistically (or Hartree–Fock–Roothaan) optimized EPs of the GTFs [11], while the second line is the result using relativistically (or DFR) optimized EPs. The PC and UCS nucleus models were adopted in the nonrelativistic and relativistic optimizations, respectively. In both optimizations, the best EPs were obtained by searching the lowest-energy points in the EP spaces referring to the total energy values only. In the table, the magnitudes of the total, $E$, potential, $V$, and correction, $W$, energies increase with increasing atomic number, $Z$. For both the nonrelativistic and the relativistic basis functions, the contribution of $W$ to the VT is not negligible especially for heavy atoms. Another aspect observed in Table 1 is that the $-(V + W)/T$ values from the relativistically optimized basis sets are very close to unity.

## 5 Conclusion and remarks

We have derived a VT in relativistic atoms with a general nuclear potential and applied it to four kinds of nuclear potentials which are currently adopted in relativistic calculations. The virial ratio consists of the usual $V/T$ term and a correction term $W/T$. Numerical calculations have shown that the $W/T$ term modifies the virial ratio $V/T$ considerably. They have also shown that the relativistic VT is useful to check the relativistic optimality of the EPs in basis sets.

We finally note that the nonrelativistic VT can be obtained immediately from Eqs. (12) and (13) by

**Table 1.** Relativistic energies and virial ratios for selected atoms. For each atom, the first line is the result using the nonrelativistically optimized wave function (Ref. [11]), while the second line is the result using the relativistically optimized wave function. For the last two atoms, relativistically optimized wave functions are not reported. $A(n)$ denotes $A \times 10^n$

| Z | Basis | $-E$ | $-V$ | $W$ | $-V/T$ | $-(V+W)/T$ |
|---|---|---|---|---|---|---|
| 2 | 6s | 2.861285098 | 5.722831202 | 3.587763(−8) | 1.00000045 | 1.00000044 |
| | | 2.861285099 | 5.722834922 | 3.588069(−8) | 0.99999980 | 0.99999979 |
| 10 | 12s8p | 1.286912043(2) | 2.576723402(2) | 7.514452(−5) | 1.00000140 | 1.00000111 |
| | | 1.286912127(2) | 2.576726732(2) | 7.532291(−5) | 1.00000030 | 1.00000001 |
| 18 | 16s11p | 5.286825096(2) | 1.061126261(3) | 1.309392(−3) | 1.00000259 | 1.00000136 |
| | | 5.286826817(2) | 1.061128612(3) | 1.322530(−3) | 1.00000125 | 1.00000001 |
| 36 | 20s15p9d | 2.788856367(3) | 5.653841348(3) | 4.519709(−2) | 1.00000984 | 1.00000184 |
| | | 2.788858943(3) | 5.653865211(3) | 4.634691(−2) | 1.00000822 | 1.00000002 |
| 54 | 22s18p12d | 7.446874164(3) | 1.535812148(4) | 4.895249(−1) | 1.00003491 | 1.00000303 |
| | | 7.446891583(3) | 1.535828923(4) | 4.904589(−1) | 1.00003198 | 1.00000004 |
| 80 | 25s18p15d10f | 1.964844414(4) | 4.228812291(4) | 7.609342 | 1.00019934 | 1.00001937 |
| | | 1.964884469(4) | 4.229259637(4) | 7.699265 | 1.00018214 | 1.00000006 |
| 86 | 25s21p15d10f | 2.360145366(4) | 5.154207965(4) | 1.393601(1) | 1.00029175 | 1.00002129 |
| 103 | 28s21p18d13f | 3.770319486(4) | 8.723497876(4) | 7.383045(1) | 1.00092503 | 1.00007790 |

replacing $T$ with $2T_{\mathrm{NR}} = \langle \phi_{\mathrm{NR}}(1) | - \sum_i \Delta_i | \phi_{\mathrm{NR}}(1) \rangle$, where $\phi_{\mathrm{NR}}(1)$ is an optimum nonrelativistic wave function.

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