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**Relativistic sum rules and integral properties of the Dirac equation**

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Relativistic generalizations are derived for the well-known nonrelativistic electric-dipole oscillator-strength sum rules. The relativistic sum rules include both positive- and negative-energy states. The derivations are valid for a Dirac electron in an arbitrary local potential. We also present a number of simple integral properties related to the relativistic virial theorem which are useful in the calculation of matrix elements.

**I. INTRODUCTION**

Sum rules of the type

$$S_k = \sum_n (E_n - E_0)^k \left| \langle \psi_0 \left| \sum_{j=1}^N \vec{r}_j \right| \psi_n \rangle \right|^2, \quad (1)$$

where  $\sum_n$  denotes summation over discrete states and integration over the continuum, are widely used in atomic-physics calculations. Nonrelativistic values  $S_k^{NR}$  have been useful in calculating moments of the oscillator strength distribution, and in constructing variation-perturbation procedures involving discrete basis sets.<sup>1-3</sup> A number of them can be calculated exactly in terms of expectation values of various operators. The well-known results for  $k=0,1,2,3$  are<sup>2,4,5</sup>

$$S_0^{NR} = \langle \psi_0 \left| \left[ \sum_{j=1}^N \vec{r}_j \right]^2 \right| \psi_0 \rangle, \quad (2)$$

$$S_1^{NR} = 3N/2, \quad (3)$$

$$S_2^{NR} = \langle \psi_0 \left| \left[ \sum_{j=1}^N \vec{\nabla}_j \right]^2 \right| \psi_0 \rangle, \quad (4)$$

$$S_3^{NR} = 2\pi Z \langle \psi_0 \left| \sum_{j=1}^N \delta(\vec{r}_j) \right| \psi_0 \rangle, \quad (5)$$

in atomic units. Here,  $Z$  is the nuclear charge and  $N$  is the number of electrons. The sum (3) is the Thomas-Reiche-Kuhn sum rule. The sums for  $k = -1$  and  $-2$  are related to the dipole polarizability<sup>5</sup> and the strength of the nonadiabatic contribution to the  $r^{-6}$  long-range electron-atom interaction potential.<sup>6,7</sup> For one-electron ions, exact values of  $S^{NR}$  have been obtained by Lamm and Szabo<sup>8</sup> for  $k = -4, -3, \dots, 3$ . The sum diverges for  $k > 3$ .

The relativistic generalization of (1) includes also an integration over the continuum of negative-energy solutions to the Dirac equation. The relativistic sum rules are useful in testing the completeness of basis sets for variational representations of the Dirac spectrum.<sup>9</sup> In this paper, we collect together a number of relativistic sum rules, together with some integral properties of the Dirac equation which are useful in relativistic calculations. The sum rules are discussed in Sec. II, and the integral properties in Sec. III.

It is also of interest to obtain the relativistic corrections for (2) to (5) for summations restricted to positive-energy states. These corrections cannot be obtained from the sum rules in this paper because the derivations require the assumption that the intermediate states form a complete set, and hence include both positive- and negative-energy states. However, numerical values can be obtained by means of relativistic variational basis sets as described in Refs. 9 and 10.

**II. ELECTRIC DIPOLE RELATIVISTIC SUM RULES WITHOUT RETARDATION**

The Dirac equation for an electron moving in a potential  $V(r)$  is

$$H\psi_n = E_n\psi_n, \quad (6)$$

where

$$H = -ic\vec{\alpha} \cdot \vec{\nabla} + \beta c^2 + V(r) \quad (7)$$

and  $\vec{\alpha}$  and  $\beta$  are the usual  $4 \times 4$  Dirac matrices. Provided that both positive- and negative-energy solutions are included, the solutions to (6) form a complete set which satisfy the closure relation

$$\sum_n |\psi_n\rangle \langle \psi_n| = 1. \quad (8)$$

In the derivations to follow, we use the notations

$$[A_i, B_j] = A_i B_j - B_j A_i,$$

$$[\vec{A}; \vec{B}] = \vec{A} \cdot \vec{B} - \vec{B} \cdot \vec{A},$$

$$\{A_i, B_j\} = A_i B_j + B_j A_i.$$

The value of  $S_0$  follows immediately from (8). It is

$$S_0 = \langle \psi_0 | r^2 | \psi_0 \rangle \quad (9)$$

as in the nonrelativistic case.

The value of  $S_1$  can be simply obtained by use of the identities

$$[\vec{r}, H] = ic \vec{\alpha}, \quad (10)$$

$$[[\vec{r}, h]; \vec{r}] = 0. \quad (11)$$

It follows that

$$\begin{aligned} S_1 &= \sum_n \langle \psi_0 | [\vec{r}, H] | \psi_n \rangle \cdot \langle \psi_n | \vec{r} | \psi_0 \rangle \\ &= \frac{1}{2} \langle \psi_0 | [[\vec{r}, H]; \vec{r}] | \psi_0 \rangle = 0. \end{aligned} \quad (12)$$

This sum rule was first obtained by Levinger *et al.*<sup>11</sup> as the relativistic generalization of the Thomas-Reiche-Kuhn sum rule. The result is zero because the contributions from positive- and negative-energy states exactly cancel. The derivation remains valid if  $\vec{r}$  is replaced by any operator  $f(\vec{r}, \vec{\nabla})$  which commutes with  $V(r)$  and the Dirac matrices  $\vec{\alpha}$  and  $\beta$ . For such operators, the general result is

$$\sum_n (E_n - E_0) | \langle \psi_0 | f(\vec{r}, \vec{\nabla}) | \psi_n \rangle |^2 = 0. \quad (13)$$

The value of  $S_2$  follows immediately from a double application of [10] with the result that

$$\begin{aligned} S_2 &= - \sum_n \langle \psi_0 | [\vec{r}, H] | \psi_n \rangle \cdot \langle \psi_n | [\vec{r}, h] | \psi_0 \rangle \\ &= - \langle \psi_0 | (ic \vec{\alpha})^2 | \psi_0 \rangle = 3c^2. \end{aligned} \quad (14)$$

The derivations of the sum rules  $S_3$ ,  $S_4$ , and  $S_5$  are somewhat more complicated.  $S_3$  can be written as the expectation value of the operator

$$A_3 = \frac{1}{2} [[\vec{r}, H]; [H, [H, \vec{r}]]]. \quad (15)$$

Using the Einstein summation convention for repeated indices, together with the properties of the

$$[H, [H, [H, \vec{r}]]] = 4ic^3 [\vec{\alpha} \vec{\nabla}^2 - (\vec{\alpha} \cdot \vec{\nabla}) \vec{\nabla}] - 2ic^2 \vec{\nabla} V \times \vec{\Sigma} + 4c^4 \beta \vec{\nabla} - 4ic^5 \vec{\alpha} \quad (27)$$

and

$$\begin{aligned} A_5 &= -16ic^5 (\vec{\alpha} \cdot \vec{\nabla}) \vec{\nabla}^2 + 4c^4 \vec{\nabla}^2 V - 4ic^4 (\vec{\nabla} V) \cdot \vec{\nabla} \times \vec{\Sigma} + 16ic^7 \vec{\alpha} \cdot \vec{\nabla} + 16c^6 \beta \vec{\nabla}^2 \\ &\quad - 8ic^5 \vec{\alpha} (\vec{\nabla} V) \beta + 8ic^7 \vec{\alpha} \cdot \vec{\nabla} - 24c^8 \beta. \end{aligned} \quad (28)$$

Dirac matrices, one obtains

$$[H, [H, x_j]] = 2ic^2 \epsilon_{jkl} \Sigma_l \frac{\partial}{\partial x_k} + 2ic^3 \alpha_j \beta, \quad (16)$$

where  $\Sigma_l$  is the  $4 \times 4$  matrix

$$\Sigma_l = \begin{pmatrix} \sigma_l & 0 \\ 0 & \sigma_l \end{pmatrix}, \quad (17)$$

and  $\epsilon_{jkl}$  is the antisymmetric symbol. Using (16), it follows that

$$A_3 = -2ic^3 \vec{\alpha} \cdot \vec{\nabla} - 6c^2 (H - V). \quad (18)$$

In addition, since  $\psi_0$  is an eigenvector of  $H$  and

$$-ic \vec{\alpha} \cdot \vec{\nabla} = [H, \vec{r} \cdot \vec{\nabla}] + \vec{r} \cdot \vec{\nabla} V, \quad (19)$$

then, for a spherically symmetric potential  $V(r)$ ,  $S_3$  reduces to

$$\begin{aligned} S_3 &= 6c^2 \langle \psi_0 | V - E_0 | \psi_0 \rangle \\ &\quad + 2c^2 \langle \psi_0 | r \frac{dV}{dr} | \psi_0 \rangle. \end{aligned} \quad (20)$$

If  $V(r)$  is a Coulomb potential  $V(r) = -Z/r$ , then this further simplifies to

$$S_3^{\text{Coul}} = -6c^2 E_0 - 4c^2 Z \langle \psi_0 | \frac{1}{r} | \psi_0 \rangle. \quad (21)$$

Similarly,  $S_4$  can be written as the expectation value of the operator

$$A_4 = \frac{1}{2} [[H, [H, \vec{r}]]; [H, [H, \vec{r}]]]. \quad (22)$$

Using (16) and the properties of the Dirac matrices, it is straightforward to obtain

$$A_4 = -8c^4 \vec{\nabla}^2 + 12c^6, \quad (23)$$

and thus

$$S_4 = -8c^4 \langle \psi_0 | \vec{\nabla}^2 | \psi_0 \rangle + 12c^6. \quad (24)$$

Finally,  $S_5$  is the expectation value of

$$A_5 = \frac{1}{2} [[H, [H, \vec{r}]]; [H, [H, [H, \vec{r}]]]]. \quad (25)$$

To evaluate  $A_5$ , we use (16) together with

$$(\vec{\Sigma} \cdot \vec{\nabla})(\vec{\Sigma} \cdot \vec{\nabla}) = \vec{\nabla}^2 \quad (26)$$

to obtain

This expression simplifies by noting that

$$[H, [H, V]] = -c^2(\vec{\nabla}^2 V) + 2ic^2(\vec{\nabla} V) \cdot \vec{\nabla} \times \vec{\Sigma} - 2ic^3 \vec{\alpha} \cdot (\vec{\nabla} V) \vec{\beta} \quad (29)$$

and that

$$i(\vec{\nabla} V) \cdot \vec{\nabla} \times \vec{\Sigma} = [\beta(\vec{\nabla} V) \cdot \vec{\nabla}, K], \quad (30)$$

where

$$K = -\beta(\vec{\Sigma} \cdot \vec{L} + 1) \quad (31)$$

is the operator whose eigenvalue is the Dirac quantum number  $\kappa$ . Then  $A_5$  reduces to

$$A_5 = 16c^4(-ic \vec{\alpha} \cdot \vec{\nabla} + \beta c^2)(\vec{\nabla}^2 - 2c^2/3) + 4c^4[\beta(\vec{\nabla} V) \cdot \vec{\nabla}, K] - 4c^2[H, [H, V]]. \quad (32)$$

Since  $\psi_0$  is an eigenvector of  $H$  and  $[H, K]=0$ , the diagonal matrix elements of the last two terms vanish and the final result for  $S_5$  is

$$S_5 = 16c^4 \langle \psi_0 | (E_0 - V) \vec{\nabla}^2 | \psi_0 \rangle - 24c^6 \langle \psi_0 | E_0 - V | \psi_0 \rangle. \quad (33)$$

$S_5$  diverges for  $ns_{1/2}$  and  $np_{1/2}$  states but not for states of higher  $|\kappa|$  because for small  $r$  the radial integrand in the second term in (33) is proportional to  $r^{2\gamma-3}$ , where  $\gamma = (\kappa^2 - \alpha^2 Z^2)^{1/2}$ .<sup>11</sup>

Values of the sum rules for the case in which  $\psi_0$  is the wave function for the ground state, together with numerical tests of these sum rules, have been given by Drake and Goldman.<sup>9</sup>

### III. INTEGRAL PROPERTIES OF THE DIRAC EIGENFUNCTIONS IN A LOCAL POTENTIAL

The bound-state solutions to the Dirac equation in a Coulomb potential satisfy a number of simple integral relations. They are useful in applications involving the calculation of matrix elements. We present in this section a derivation of the integral relations valid for Coulomb potentials, together with more general formulas valid for arbitrary local potentials.

The solutions to Dirac's equation in a central potential can be written in the form<sup>11</sup>

$$\psi = \begin{pmatrix} i \frac{g(r)}{r} \Omega_{jIM} \\ -\frac{f(r)}{r} \Omega_{\tilde{j}IM} \end{pmatrix}, \quad (34)$$

where  $\tilde{l} = 2j - l$  and  $\Omega_{jIM}$  is a two-component spherical spinor defined as the vector-coupled product

$$\Omega_{jIM} = \sum_{m, \mu} \langle lm \frac{1}{2} \mu | jM \rangle Y_l^m(\theta, \phi) \chi_\mu, \quad (35)$$

with

$$\chi_{1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \chi_{-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

The large and small radial functions  $g(r)$  and  $f(r)$  satisfy the equations

$$\begin{aligned} g' + \frac{\kappa}{r} g - \left[ \alpha E + \alpha V + \frac{1}{\alpha} \right] f &= 0, \\ g' - \frac{\kappa}{r} f + \left[ \alpha E + \alpha V - \frac{1}{\alpha} \right] g &= 0, \end{aligned} \quad (36)$$

together with the boundary conditions  $g(r) \rightarrow 0$  and  $f(r) \rightarrow 0$  as  $r \rightarrow 0$  and  $r \rightarrow \infty$ . Here,  $\alpha$  is the fine-structure constant ( $\alpha = 1/c$  in atomic units). The normalization condition is

$$\int_0^\infty (g^2 + f^2) dr = 1. \quad (37)$$

The integral relations to be derived below are as follows. In atomic units

$$\langle \beta \vec{\alpha} \cdot \vec{p} \rangle = 0, \quad (38)$$

$$c^2 \langle \beta \rangle = E - \langle \hat{r} \cdot \vec{\nabla}(rV) \rangle, \quad (39)$$

$$c^2 \langle \beta V \rangle = E^2 - c^4 - E \langle \hat{r} \cdot \vec{\nabla}(rV) \rangle, \quad (40)$$

$$\langle \vec{\alpha} \cdot \vec{r} \rangle = 0, \quad (41)$$

$$c^3 \langle \beta \vec{\alpha} \cdot \vec{r} \rangle = \frac{i}{2} [c^2 - 2\kappa E + 2\kappa E + 2\kappa \langle \hat{r} \cdot \vec{\nabla}(rV) \rangle], \quad (42)$$

$$c^3 \langle \beta \vec{\alpha} \cdot \vec{r} V \rangle = i\kappa(c^4 - E^2) + \frac{i}{2}(2\kappa E + c^2) \langle \hat{r} \cdot \vec{\nabla}(rV) \rangle, \quad (43)$$

where  $\kappa$  is the Dirac quantum number. The last two equations which contain  $\kappa$  are valid only for a

central potential  $V(r)$ . The formulas further simplify for a Coulomb potential  $V = -Z/r$  because then  $\hat{r} \cdot \vec{\nabla}(rV) = 0$ . The first three equations in this limiting Coulomb case were obtained previously by Rose and Welton.<sup>12</sup>

The derivations of the above equations are related to the relativistic generalization of the virial

theorem. Taking matrix elements of (19) yields

$$c \langle \psi_m | \vec{\alpha} \cdot \vec{p} | \psi_n \rangle = (E_m - E_n) \langle \psi_m | \vec{r} \cdot \vec{\nabla} | \psi_n \rangle + \langle \psi_m | \vec{r} \cdot \vec{\nabla} V | \psi_n \rangle. \quad (44)$$

The diagonal matrix elements of (44) are

$$c \langle \vec{\alpha} \cdot \vec{p} \rangle = \langle \vec{r} \cdot \vec{\nabla} V \rangle, \quad (45)$$

which is the relativistic virial theorem.<sup>12-14</sup> Using (19) to replace  $c \vec{\alpha} \cdot \vec{p}$  in the Dirac equation (6) and taking matrix elements yields

$$c^2 \langle \psi_m | \beta | \psi_n \rangle = E_n \delta_{m,n} + (E_n - E_m) \langle \psi_m | \vec{r} \cdot \vec{\nabla} | \psi_n \rangle - \langle \psi_m | \hat{r} \cdot \vec{\nabla}(rV) | \psi_n \rangle. \quad (46)$$

The diagonal matrix elements of (46) give Eq. (39). The matrix elements of the identity

$$\frac{1}{2}(H\beta + \beta H) = c^2 + \beta V \quad (47)$$

together with (46) yield

$$c^2 \langle \psi_m | \beta V | \psi_n \rangle = (E_n^2 - c^4) \delta_{m,n} + \frac{1}{2}(E_n^2 - E_m^2) \langle \psi_m | \vec{r} \cdot \vec{\nabla} | \psi_n \rangle - \frac{1}{2}(E_n + E_m) \langle \psi_m | \hat{r} \cdot \vec{\nabla}(rV) | \psi_n \rangle, \quad (48)$$

which reduces to Eq. (40). Using

$$\langle \psi_m | \beta H | \psi_n \rangle = \langle \psi_m | \beta E_n | \psi_n \rangle \quad (49)$$

together with (46) and (48) yields

$$c^3 \langle \psi_m | \beta \vec{\alpha} \cdot \vec{p} | \psi_n \rangle = \frac{1}{2}(E_n - E_m)^2 \langle \psi_m | \vec{r} \cdot \vec{\nabla} | \psi_n \rangle - \frac{1}{2}(E_n - E_m) \langle \psi_m | \hat{r} \cdot \vec{\nabla}(rV) | \psi_n \rangle, \quad (50)$$

which reduces to Eq. (38). The above equation is equivalent to

$$c \langle \psi_m | \beta \vec{\alpha} \cdot \vec{p} | \psi_n \rangle = \frac{1}{2}(E_n - E_m) \langle \psi_m | \beta | \psi_n \rangle, \quad (51)$$

which also follows directly from the operator identity<sup>12</sup>

$$[\beta, H] = 2c\beta \vec{\alpha} \cdot \vec{p}. \quad (52)$$

Equation (41) is simply obtained by taking diagonal matrix elements of

$$[r^2, H] = 2ic \vec{\alpha} \cdot \vec{r}. \quad (53)$$

The last two integral relations (42) and (43) are valid only for states of definite  $\kappa$ . Using (53), the operator  $K$  defined by (31) can be written in the form

$$K = \frac{\beta}{4c^2} [H, [H, r^2]] + ic(\vec{\alpha} \cdot \vec{r}) + \frac{1}{2}\beta. \quad (54)$$

Taking matrix elements of  $\beta K$  and using (46) for matrix elements of  $\beta$  leads to

$$ic^3 \langle \psi_m | \beta \vec{\alpha} \cdot \vec{r} | \psi_n \rangle = \left[ \kappa E_n - \frac{c^2}{2} \right] \delta_{m,n} - \frac{(E_m - E_n)^2}{4} \langle \psi_m | r^2 | \psi_n \rangle + \kappa(E_n - E_m) \langle \psi_m | \vec{r} \cdot \vec{\nabla} | \psi_n \rangle - \kappa \langle \psi_m | \hat{r} \cdot \vec{\nabla}(rV) | \psi_n \rangle. \quad (55)$$

The diagonal matrix elements reduce to Eq. (42). The last of the integral relations requires, in addition, the anticommutator identity

$$\{\beta K, H\} = \frac{1}{4c^2} \{H[H, [H, r^2]]\} + ic\{H, \beta(\vec{\alpha} \cdot \vec{r})\} + H, \quad (56)$$

with

$$\{H, \beta(\vec{\alpha} \cdot \vec{r})\} = -2icK + ic\beta + 2\beta(\vec{\alpha} \cdot \vec{r})V. \quad (57)$$

Taking matrix elements and again using (46) for matrix elements of  $\beta$  yields

$$2ic^3 \langle \psi_m | \beta \vec{\alpha} \cdot \vec{r} V | \psi_n \rangle = 2\kappa(E_n^2 - c^4) \delta_{m,n} - \frac{1}{4}(E_m + E_n)(E_m - E_n)^2 \langle \psi_m | r^2 | \psi_n \rangle \\ + [\kappa(E_m + E_n) + c^2] [(E_m - E_n) \langle \psi_m | \vec{r} \cdot \vec{\nabla} | \psi_n \rangle - \langle \psi_m | \hat{r} \cdot \vec{\nabla}(rV) | \psi_n \rangle], \quad (58)$$

which reduces to Eq. (43).

For the case of a Coulomb potential, the above results expressed in terms of radial integrals become remarkably simple. Using (39) through (43), together with the normalization condition (37), we obtain (in atomic units)

$$\int_0^\infty g^2 dr = \frac{1}{2}(1 + \alpha^2 E), \quad (59)$$

$$\int_0^\infty f^2 dr = \frac{1}{2}(1 - \alpha^2 E), \quad (60)$$

$$\int_0^\infty fg dr = \frac{\kappa}{2\alpha Z} [1 - (\alpha^2 E)^2], \quad (61)$$

$$\int_0^\infty fgr dr = \frac{\alpha}{4} (2\kappa\alpha^2 E - 1), \quad (62)$$

$$\int_0^\infty \frac{dr}{r} (g^2 - f^2) = \frac{1}{\alpha^2 Z} [1 - (\alpha^2 E)^2], \quad (63)$$

valid for any bound-state solution to the Dirac equation with a Coulomb potential  $V(r) = -Z/r$ . Since  $E$  includes the rest mass energy,

$$\alpha^2 E \simeq 1 - (\alpha Z)^2 / 2n^2.$$

#### ACKNOWLEDGMENTS

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