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Relativistic Effects in Atomic Fine Structure*

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ABSTRACT

Operators are obtained which can be evaluated with respect to nonrelativistic wave functions to produce the same result as obtained by evaluating the Breit equation with respect to relativistic wave functions. This greatly simplifies calculations involving the Breit equation by allowing the calculations to be made within the more familiar framework of nonrelativistic theory. The operators are classified according to their angular dependence; a comparison with the angular dependence of each fine-structure operator leads to the relativistic equivalents of the fine-structure interactions. The operators are expanded in a power series in $(v/c)^2$, and the lowest nonvanishing terms are shown to be the fine-structure interactions.

We have obtained equivalent operators for the terms in the Breit equation (Sec. III); these operators are then broken up into groups which correspond to fine-structure interactions (Sec. IV). Finally, these groups are reduced to the nonrelativistic limit in order to obtain the fine-structure interactions. This last step is important because it reveals new operators of the same magnitude as the fine-structure interactions.

II. THE HAMILTONIAN

The analysis is based on the solution by first-order perturbation theory of the Breit equation for two electrons (charge -e),[4, 5]

$$\mathcal{H}\,\Psi = \left\{ \sum_{i=1,2} \left[\underset{\sim}{\alpha}_i \cdot (c\underset{\sim}{p}_i + e\underset{\sim}{A}_i) + \beta_i mc^2 - \frac{Ze^2}{r_i} \right] + \frac{e^2}{r_{12}} - \frac{e^2}{2}\,\frac{\underset{\sim}{\alpha}_1 \cdot \underset{\sim}{\alpha}_2}{r_{12}} \right.$$

$$\left. - \frac{e^2}{2}\,\frac{(\underset{\sim}{\alpha}_1 \cdot \underset{\sim}{r}_{12})(\underset{\sim}{\alpha}_2 \cdot \underset{\sim}{r}_{12})}{r_{12}^3} \right\} \Psi \qquad (1)$$

$$= E\Psi \,.$$

We assume that the potential terms in Eq. (1) can be approximately replaced by a central field term $\sum_i U(r_i)$. The approximate Hamiltonian is then

$$\mathcal{H}_0 = \sum_{i=1,2} \left[\underset{\sim}{\alpha}_i \cdot (c\underset{\sim}{p}_i + e\underset{\sim}{A}_i) + \beta_i mc^2 + U(r_i) \right] , \qquad (2)$$

and the difference, $\mathcal{H}_1 = \mathcal{H} - \mathcal{H}_0$, can be treated as a perturbation. For the special case in which $\underset{\sim}{A}_i = 0$, the wave function satisfying

$$\mathcal{H}_0 \Psi_0 = E_0 \Psi_0 = (E_0^1 + E_0^2)\Psi_0 \,, \qquad (3)$$

where E^i is the energy of electron i, can be written as a product of wave functions of the form

$$|\ell jm) = \begin{pmatrix} F/r\,|\ell jm\rangle \\ iG/r\,|\bar{\ell} jm\rangle \end{pmatrix} , \qquad (4)$$

where $\bar{\ell} = \ell \pm 1$ as $j = \ell \pm 1/2$,

and

$$|\ell jm\rangle = \sum_{m_\ell m_s} (-)^{\ell - 1/2 - m} [j]^{1/2} \begin{pmatrix} 1/2 & \ell & j \\ m_s & m_\ell & -m \end{pmatrix} |\ell m_\ell\rangle\, \chi^{1/2}_{m_s} \,. \qquad (5)$$

The term $\chi^{1/2}$ is the usual two-component spinor. Here and in what follows, relativistic wave functions are written in the general form $|\ell jm)$ and nonrelativistic functions as $|\ell jm\rangle$. Terms written $[a, b, \cdots]$ stand for $(2a+1)(2b+1)\cdots$. We shall restrict our discussion to the configuration ℓ^2.

The radial functions F and G, which can be taken to be real, can be related through Eqs. (2), (3), and (4):

$$\left(\frac{d}{dr_i} - \frac{\kappa_i}{r_i}\right) F_i = \frac{1}{\hbar c}\left[mc^2 + E_0^i - U(r_i)\right] G_i ,$$

$$\left(\frac{d}{dr_i} + \frac{\kappa_i}{r_i}\right) G_i = \frac{1}{\hbar c}\left[mc^2 - E_0^i + U(r_i)\right] F_i , \tag{6}$$

with $\kappa_i = (-)^{j_i+\ell-1/2} \frac{[j_i]}{2}$.

The energy, to the first order in the perturbation, is then given by

$$(\Psi_0|\mathcal{H}_0 + \mathcal{H}_1|\Psi_0) = (E_0 + E_1)(\Psi_0|\Psi_0) = E(\Psi_0|\Psi_0)$$

$$= (\Psi_0|\underset{\sim}{\alpha}\cdot\underset{\sim}{p} + \beta mc^2 + \mathcal{H}_\alpha + \mathcal{H}_\beta + \mathcal{H}_\gamma + \mathcal{H}_\delta|\Psi_0), \tag{7}$$

where

$$\mathcal{H}_\alpha = \sum_i \mathcal{H}_\alpha^i$$

$$\mathcal{H}_\alpha^i = -\frac{Ze^2}{r_i} ,$$

$$\mathcal{H}_\beta = \frac{e^2}{r_{12}} ,$$

$$\mathcal{H}_\gamma = -\frac{e^2}{2}\frac{\underset{\sim}{\alpha}_1\cdot\underset{\sim}{\alpha}_2}{r_{12}}$$

and

$$\mathcal{H}_\delta = -\frac{e^2}{2}\frac{(\underset{\sim}{\alpha}_1\cdot\underset{\sim}{r}_{12})(\underset{\sim}{\alpha}_2\cdot\underset{\sim}{r}_{12})}{r_{12}^3} .$$

The first two terms on the extreme right-hand side of Eq. (7) are the kinetic energy and mass-effect terms, respectively. In the following sections, we shall not be directly concerned with these two terms, but rather with the remaining terms in $\mathcal{H}$.

III. EQUIVALENT OPERATORS

We wish to obtain the operator O_E defined by the equation

$$(\Psi_0|\mathcal{H}_\alpha + \mathcal{H}_\beta + \mathcal{H}_\gamma + \mathcal{H}_\delta|\Psi_0) = \langle \Psi | O_E | \Psi \rangle , \tag{8}$$

where $|\Psi\rangle$ is the nonrelativistic wave function which $|\Psi_0)$ approaches in the nonrelativistic limit. The operator O_E is the "equivalent operator" for the interactions $\mathcal{H}_\alpha$ through $\mathcal{H}_\delta$, and will be obtained below by considering the interactions $\mathcal{H}_\alpha$ through $\mathcal{H}_\delta$ separately.

A. Equivalent Operator for $\mathcal{H}_\alpha$

Evaluation of $\mathcal{H}_\alpha^i$ between relativistic wave functions is straightforward, and yields

$$(\ell jm|\mathcal{H}_\alpha^i|\ell jm) = -Ze^2 \int \frac{(F_j^2 + G_j^2)_i}{r_i} \, dr_i \; . \tag{9}$$

The equivalent operator for $\mathcal{H}_\alpha^i$, namely O_α^i , can be written in the general form

$$O_\alpha^i = \sum_{\kappa k K} a^i(\kappa k K) \underset{\sim}{w}_i^{(\kappa k)K}, \tag{10}$$

where the a are constants to be determined, and the $\underset{\sim}{w}^{(\kappa k)K}$ are defined by the relation

$$\underset{\sim}{w}^{(\kappa k)K} = \{\underset{\sim}{t}^\kappa \underset{\sim}{v}^k\}^K,$$

$$\langle s||\underset{\sim}{t}^\kappa||s\rangle = [\kappa]^{1/2}, \tag{11}$$

and

$$\langle \ell ||v^k||\ell'\rangle = \delta_{\ell\ell'} [k]^{1/2}.$$

Because $\mathcal{H}_\alpha$ is a scalar, $K = 0$ in Eq. (10) above, and therefore $\kappa = k$. Taking matrix elements, we obtain

$$\left\langle \ell jm \middle| O_\alpha^i \middle| \ell jm \right\rangle = \sum_k \alpha^i(kk)(-)^{k+\ell+j+1/2}[k]^{1/2} \begin{Bmatrix} 1/2 & 1/2 & k \\ \ell & \ell & j \end{Bmatrix} . \quad (12)$$

Equating the right-hand sides of Eqs. (9) and (12), and multiplying both sides by

$$\sum_j \begin{Bmatrix} 1/2 & \ell & j \\ \ell & 1/2 & k \end{Bmatrix} [j](-)^j ,$$

we obtain

$$\alpha^i(kk) = [k]^{1/2}(-)^{k+\ell-1/2} Ze^2 \sum_j [j] (-)^j \begin{Bmatrix} 1/2 & \ell & j \\ \ell & 1/2 & k \end{Bmatrix} \int_0^\infty \frac{\left(F_j^2 + G_j^2\right)_i}{r_i} dr_i . \quad (13)$$

We postpone a discussion of this and subsequent results until Sec. IV.

B. Equivalent Operator for $\mathcal{H}_\beta$

Because $\mathcal{H}_\beta$ is a two-body operator, we must consider matrix elements between relativistic states composed of two electrons. The final form obtained for O_E does not depend on the type of coupling used for the wave function. However, in order to demonstrate more fully the method to be used, we use below wave functions of the form $|\ell^2 SLJM)$.

As is apparent from Eq. (4), in relativistic theory j, and not ℓ, is a good quantum number. The state $|\ell^2 SLJM)$ must then be decomposed into states $|j_1 j_2 JM)$, which in turn are decomposed in the usual way into a sum of products of $|\ell j_1 m_1)$ and $|\ell j_2 m_2)$. Then

$$(\ell^2 S_1 L_1 JM|\mathcal{H}_\beta|\ell^2 S_2 L_2 JM) = \sum_{\substack{j_1 j_2\\ j_3 j_4}} \left[S_1, L_1, S_2, L_2, j_1, j_2, j_3, j_4\right]^{1/2}$$

$$\times \begin{Bmatrix} 1/2 & 1/2 & S_1 \\ \ell & \ell & L_1 \\ j_1 & j_2 & J \end{Bmatrix} \begin{Bmatrix} 1/2 & 1/2 & S_2 \\ \ell & \ell & L_2 \\ j_3 & j_4 & J \end{Bmatrix} (j_1 j_2 JM|\mathcal{H}_\beta|j_3 j_4 JM). \tag{14}$$

The term $\mathcal{H}_\beta$ can be expanded as

$$e^2 \sum_K \frac{r_<^K}{r_>^{K+1}} \underset{\sim}{C}_1^K \cdot \underset{\sim}{C}_2^K .$$

The symbol C^K is defined by

$$C_m^K = (4\pi/2K+1)^{1/2} Y_m^K$$

where Y_m^K is the usual spherical harmonic. In evaluating the matrix element on the right side of Eq. (14), one obtains reduced matrix elements such as

$$(j_1||C^K r^K||j_3) = \left\langle \ell j_1||C^K||\ell j_3\right\rangle \int F_{j_1} F_{j_3} r^K dr + \left\langle \bar{\ell} j_1||C^K||\bar{\ell} j_3\right\rangle \int G_{j_1} G_{j_3} r^K dr. \tag{15}$$

This simplifies to

$$= (-)^{j_3 - 1/2} [j_1, j_3]^{1/2} \begin{pmatrix} j_1 & K & j_3 \\ -1/2 & 0 & 1/2 \end{pmatrix} \int (F_{j_1} F_{j_3} + G_{j_1} G_{j_3}) r^K dr$$

for K even, or zero for K odd. We finally obtain, for Eq. (14),

$$(\ell^2 S_1 L_1 JM|\mathcal{H}_\beta|\ell^2 S_2 L_2 JM) = e^2 \sum [S_1, S_2, L_1, L_2]^{1/2} [j_1, j_2, j_3, j_4] (-)^{j_1+j_3+J}$$

$$\times \begin{Bmatrix} 1/2 & 1/2 & S_1 \\ \ell & \ell & L_1 \\ j_1 & j_2 & J \end{Bmatrix} \begin{Bmatrix} 1/2 & 1/2 & S_2 \\ \ell & \ell & L_2 \\ j_3 & j_4 & J \end{Bmatrix} \begin{Bmatrix} j_3 & j_4 & J \\ j_2 & j_1 & K \end{Bmatrix} \begin{pmatrix} j_1 & K & j_3 \\ -1/2 & 0 & 1/2 \end{pmatrix} \begin{pmatrix} j_2 & K & j_4 \\ -1/2 & 0 & 1/2 \end{pmatrix}$$

$$\times \iint (F_1 F_3 + G_1 G_3)_1 (F_2 F_4 + G_2 G_4)_2 \frac{r_<^K}{r_>^{K+1}} dr_1 dr_2, \quad (16)$$

where the sum is over j_1, j_2, j_3, j_4, and K, and F_1 has been written for F_{j_1}, etc. Particle assignments are subscripted to the parentheses.

The equivalent operator is written in this case as

$$O_\beta = \sum \beta(k_1 K_1 k_2 K_2 k) \; \underset{\sim}{w}_1^{(k_1 K_1)k} \cdot \underset{\sim}{w}_2^{(k_2 K_2)k} , \quad (17)$$

where the sum is over k_1, K_1, k_2, K_2, and k. This is the most general form for a scalar two-body interaction. Proceeding as in Sec. IIIA, we evaluate

$$\left\langle \ell^2 S_1 L_1 JM | O_\beta | \ell^2 S_2 L_2 JM \right\rangle$$

and equate the results with Eq. (16). The constant β is obtained by utilizing the orthogonality conditions for 6-j and 9-j symbols. One obtains

$$\beta(k_1 K_1 k_2 K_2 k) = e^2 \sum_{\substack{j_1 j_2 \\ j_3 j_4}} (-)^{j_4+j_3+1} \frac{[k_1, K_1, k_2, K_2]^{1/2}}{[k]} [j_1, j_2, j_3, j_4]$$

$$\times \begin{Bmatrix} 1/2 & 1/2 & k_1 \\ \ell & \ell & K_1 \\ j_1 & j_3 & k \end{Bmatrix} \begin{Bmatrix} 1/2 & 1/2 & k_2 \\ \ell & \ell & K_2 \\ j_2 & j_4 & k \end{Bmatrix} \begin{pmatrix} j_1 & k & j_3 \\ 1/2 & 0 & -1/2 \end{pmatrix} \begin{pmatrix} j_2 & k & j_4 \\ 1/2 & 0 & -1/2 \end{pmatrix} \quad (18)$$

$$\times \iint (F_1 F_3 + G_1 G_3)_1 \; (F_2 F_4 + G_2 G_4)_2 \frac{r_<^k}{r_>^{k+1}} dr_1 dr_2 ,$$

where k is even. By interchanging j_1 and j_3, j_2 and j_4, we see that β will be zero for either (or both) $k_1 + K_1$ or $k_2 + K_2$ odd.

C. Equivalent Operator for $\mathcal{H}_\gamma$

The derivation of the equivalent operator for $\mathcal{H}_\gamma$ is carried out in essentially the same manner as for the equivalent operator for $\mathcal{H}_\beta$. We first, however, rewrite $\mathcal{H}_\gamma$:

$$\mathcal{H}_\gamma = -\frac{e^2}{2}\frac{\underset{\sim}{\alpha}_1\cdot\underset{\sim}{\alpha}_2}{r_{12}} = -\frac{e^2}{2}\sum_\beta(\underset{\sim}{\alpha}_1\cdot\underset{\sim}{\alpha}_2)(\underset{\sim}{C}_1^\beta\cdot\underset{\sim}{C}_2^\beta)\frac{r_<^\beta}{r_>^{\beta+1}}$$

$$= -\frac{e^2}{2}\sum_{k\beta}(\underset{\sim}{\alpha}_1\underset{\sim}{C}_1^\beta)^k\cdot(\underset{\sim}{\alpha}_2\underset{\sim}{C}_2^\beta)^k(-)^{1+k+\beta}\frac{r_<^\beta}{r_>^{\beta+1}}\,. \tag{19}$$

Then

$$(\ell^2S_1L_1JM|\mathcal{H}_\gamma|\ell^2S_2L_2JM) = -\frac{e^2}{2}\sum[j_1,j_2,j_3,j_4,L_1,L_2,S_1,S_2]^{1/2}(-)^{j_2+j_3+J+k}$$

$$\times\begin{Bmatrix}1/2 & 1/2 & S_1\\ \ell & \ell & L_1\\ j_1 & j_3 & J\end{Bmatrix}\begin{Bmatrix}1/2 & 1/2 & S_2\\ \ell & \ell & L_2\\ j_2 & j_4 & J\end{Bmatrix}\begin{Bmatrix}j_3 & j_4 & J\\ j_2 & j_1 & k\end{Bmatrix} \tag{20}$$

$$\times\iint(j_1||(\underset{\sim}{\alpha}\underset{\sim}{C}^\beta)^k||j_3)(j_2||(\underset{\sim}{\alpha}\underset{\sim}{C}^\beta)^k||j_4)\frac{r_<^\beta}{r_>^{\beta+1}}\,dr_1dr_2\,.$$

The sum is over j_1, j_2, j_3, j_4, β, and k; the reduced matrix elements are given by

$$(j_1||(\underset{\sim}{\alpha}C^{\beta})^k||j_3) = i[k, j_1, j_3]^{1/2} \left\{ \sqrt{2}\,(-)^{\ell+1} \begin{pmatrix} 1 & \beta & k \\ -1 & 0 & 1 \end{pmatrix} \begin{pmatrix} j_1 & j_3 & k \\ -1/2 & -1/2 & 1 \end{pmatrix} (F_1G_3+G_3F_1) \right.$$

$$\left. + (-)^{j_3+1/2} \begin{pmatrix} 1 & \beta & k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_1 & j_3 & k \\ -1/2 & 1/2 & 0 \end{pmatrix} (F_1G_3 - G_1F_3) \right\} \qquad (21)$$

for β odd, zero for β even. The equivalent operator is defined as

$$O_\gamma = \sum \gamma(k_1K_1k_2K_2k)\, \underset{\sim}{w}_1^{(k_1K_1)k} \cdot \underset{\sim}{w}_2^{(k_2K_2)k}, \qquad (22)$$

where the sum is over k_1, K_1, k_2, K_2, and k. Solving for γ, we find

$$\gamma(k_1K_1k_2K_2k) = -\frac{e^2}{2} \sum [j_1, j_2, j_3, j_4]^{1/2} \frac{[k_1,K_1,k_2,K_2]^{1/2}}{[k]} (-)^k$$

$$\times \begin{Bmatrix} 1/2 & 1/2 & k_1 \\ \ell & \ell & K_1 \\ j_1 & j_3 & k \end{Bmatrix} \begin{Bmatrix} 1/2 & 1/2 & k_2 \\ \ell & \ell & K_2 \\ j_2 & j_4 & k \end{Bmatrix} \qquad (23)$$

$$\times \iint (j_1||(\underset{\sim}{\alpha}_1\, \underset{\sim}{C}_1{}^{\beta})^k||j_3)(j_2||(\underset{\sim}{\alpha}_2\underset{\sim}{C}_2{}^{\beta})^k||j_4)\, \frac{r_<^{\beta}}{r_>^{\beta+1}}\, dr_1dr_2 .$$

By interchanging j_1 and j_3, j_2 and j_4, we see that γ is zero if either (or both) $k_1 + K_1$ or $k_2 + K_2$ is even.

D. Equivalent Operator for $\mathcal{H}_\delta$

The term $\mathcal{H}_\delta$ can be rewritten in the form

$$\mathcal{H}_\delta = -\frac{e^2}{2}\left[\frac{1}{3}\frac{\underset{\sim}{a}_1\cdot\underset{\sim}{a}_2}{r_{12}} + (5)^{1/2}\frac{((\underset{\sim}{a}_1\underset{\sim}{a}_2)^2(\underset{\sim}{r}_{12}\underset{\sim}{r}_{12})^2)^0}{r_{12}^3}\right]. \quad (24)$$

The first term on the right above has the same form as $\mathcal{H}_\gamma$; the second term can be evaluated by using the relationship[7]

$$\frac{(\underset{\sim}{r}_{12}\underset{\sim}{r}_{12})^2}{r_{12}^3} = \sum_\beta (-)^\beta \frac{r_<^\beta}{r_>^{\beta+1}}\left\{(\underset{\sim}{C}_1^\beta\underset{\sim}{C}_2^\beta)^2\left[\frac{(8\beta)(\beta+1)(2\beta+1)}{(15)(2\beta-1)(2\beta+3)}\right]^{1/2}\right.$$

$$- (\underset{\sim}{C}_1^{\beta-2}\underset{\sim}{C}_2^\beta)^2\left[\frac{(\beta)(\beta-1)(2\beta-3)(2\beta+1)}{5(2\beta-1)}\right]^{1/2} \quad (25)$$

$$\left. + (\underset{\sim}{C}_1^\beta\underset{\sim}{C}_2^{\beta+2})^2\left[\frac{(\beta+1)(\beta+2)(2\beta+1)(2\beta+5)}{5(2\beta+3)}\right]^{1/2}\right\}.$$

The terms in this expansion can be rewritten

$$F(\beta\gamma)(-)^\beta\left\{(\underset{\sim}{a}_1\underset{\sim}{a}_2)^2(\underset{\sim}{C}_1^\beta\underset{\sim}{C}_2^\gamma)^2\right\}^0 = \sum_K (-)^1 (5)^{1/2}\begin{Bmatrix}1 & 1 & 2\\ \gamma & \beta & K\end{Bmatrix}\left((\underset{\sim}{a}_1\underset{\sim}{C}_1^\beta)^K\cdot(\underset{\sim}{a}_2\underset{\sim}{C}^\gamma)^K\right)F(\beta\gamma), \quad (26)$$

where $\gamma = \beta,\ \beta \pm 2$, and $F(\beta\gamma)$ is the term multiplying the angular factor $(\underset{\sim}{C}^\beta\underset{\sim}{C}^\gamma)^2$ in Eq. (25). Upon inserting Eq. (26) into Eq. (24), one sees that $\mathcal{H}_\delta$ has the same form as $\mathcal{H}_\gamma$. We write the equivalent operator for $\mathcal{H}_\delta$ as

$$O_\delta = \sum\left\{\delta^0(k_1K_1k_2K_2k) + \delta^2(k_1K_1k_2K_2k)\right\}\left(\underset{\sim}{w}_1^{(k_1K_1)k}\cdot\underset{\sim}{w}_2^{(k_2K_2)k}\right) \quad (27)$$

where the sum is over k_1, K_1, k_2, K_2, and k. The expression δ^0 corresponds to the first term on the right of Eq. (24), δ^2 to the second. These two expressions are easily evaluated by comparison with Eqs. (19) and (23). One obtains

$$\delta^0(k_1K_1k_2K_2k) = \frac{1}{3}\,\gamma(k_1K_1k_2K_2k) \tag{28}$$

and

$$\delta^2(k_1K_1k_2K_2k) = -\frac{[2]e^2}{2}\sum \frac{[j_1, j_2, j_3, j_4, k_1, K_1, k_2, K_2]^{1/2}}{[k]}(-)^\beta$$

$$\times \begin{Bmatrix} 1/2 & 1/2 & k_1 \\ \ell & \ell & K_1 \\ j_1 & j_3 & k \end{Bmatrix} \begin{Bmatrix} 1/2 & 1/2 & k_2 \\ \ell & \ell & K_2 \\ j_2 & j_4 & k \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 2 \\ \gamma & \beta & k \end{Bmatrix} F(\gamma\beta) \tag{29}$$

$$\times \iint (j_1||(a_1C_1^{\beta})^k||j_3)(j_2||(a_2C_2^{\gamma})^k||j_4)\,\frac{r_<^{\beta}}{r_>^{\beta+1}}\,dr_1dr_2\,.$$

The sum is over j_1, j_2, j_3, j_4, β, and γ. Both δ^0 and δ^2 are zero if β is even, and if either (or both) $k_1 + K_1$ or $k_2 + K_2$ is even.

Further simplification can be obtained for particular cases: let $\delta^2 = \delta^{21} + \delta^{22} + \delta^{23}$, where δ^{21} stands for the case in which $\gamma = \beta$, δ^{22} for $\gamma = \beta + 2$, and δ^{23} for $\gamma = \beta - 2$. For k odd, $\delta^{21} = \frac{2}{3}\gamma$, δ^{22} and δ^{23} are zero. In this case $\delta^0 + \delta^2 = \gamma$. For k even and $k = \beta + 1$,

$$\delta^0 + \delta^{21} + \gamma = \frac{2(k+1)}{2k+1}\,\gamma\,;$$

for k even and $k = \beta - 1$,

$$\delta^0 + \delta^{21} + \gamma = \frac{2k}{2k+1}\,\gamma\,.$$

No analogous simplifications are possible for δ^{22} or δ^{23}.

IV. INTERPRETATION OF THE OPERATORS

The terms in O_E^- having the same angular dependence as the fine-structure interactions can be identified as relativistic fine-structure interactions. These relativistic interactions can be expanded in a power series in orders of $(v/c)^2$; the lowest nonvanishing terms will, in most instances, be just the usual fine-structure interactions. We consider now the terms according to their angular dependence.

A. Terms With No Angular Dependence

The only term of interest here is $\alpha(00)$; $\beta(00000)$, the only other nonzero term having no angular dependence, will be seen to be the first term in the expansion of the operator e^2/r_{12}:

$$\alpha^i(00)W^{(00)0} =$$

$$- \frac{Ze^2}{2[\ell]} \left([\ell + 1/2] \int \frac{(F_+^2 + G_+^2)_i}{r_i} dr_i + [\ell - 1/2] \int \frac{(F_-^2 + G_-^2)_i}{r_i} \right) dr_i \tag{30}$$

where $F_\pm$ stands for $F_{j=\ell\pm1/2}$, etc.

The expansion of Eq. (30) in orders of $(v/c)^2$ is based on Eq. (6). We define $E_0^i = W^i + mc^2$, and write Eq. (6) as

$$G_i = \frac{\hbar}{2mc} \left\{ 1 + \frac{W^i - U(r_i)}{2mc^2} \right\}^{-1} \left(\frac{d}{dr_i} - \frac{\kappa}{r_i} \right) F_i \,. \tag{31}$$

The expansion of the expression in braces in powers of $\frac{W - U}{2mc^2}$ is roughly equivalent to an expansion in orders $(v/c)^2$. We will need to consider only the first term in the expansion

$$G_i = \frac{\mu_0}{e} \left(\frac{d}{dr_i} - \frac{\kappa}{r_i} \right) F_i \,, \tag{32}$$

where $\mu_0 = \dfrac{e\hbar}{2\,mc}$.

To this order, F satisfies the equation

$$\left[-\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2}-\frac{\ell(\ell+1)}{r^2}\right)+U(r)\right]F_i = W^i F_i \tag{33}$$

for both $j = \ell + 1/2$ and $j = \ell - 1/2$ states; Eq. (33) is just the radial Schrödinger wave equation for a particle in a central field. The normalization used in this limit is $\int F^2 dr = 1$.

In this order of approximation, the term containing F^2 in Eq. (30) becomes

$$-Ze^2\int \frac{F_i^2}{r_i^2}\,dr_i\,. \tag{34}$$

The term in G^2 can be obtained by use of a general relationship obtained from Eq. (32),

$$\int GVG dr = \frac{\mu_0^2}{e^2}\int F\left\{-\frac{dV}{dr}\frac{dF}{dr}+\left[\frac{\kappa}{r}\frac{dV}{dr}-V\left(\frac{d^2}{dr^2}-\frac{\ell(\ell+1)}{r^2}\right)\right]F\right\}dr, \tag{35}$$

where V is any function of r. The term containing G^2 then becomes

$$\frac{\mu_0^2}{e^2}\int F\left[\frac{1}{2}\nabla^2\left(-\frac{Ze^2}{r_i}\right)+\frac{Ze^2}{r_i}\left(\frac{d^2}{dr_i^2}-\frac{\ell(\ell+1)}{r_i^2}\right)\right]F_i dr_i. \tag{36}$$

This term is discussed further in the next section.

B. Coulomb Repulsion Terms

The Coulomb repulsion Hamiltonian, e^2/r_{12}, can be written as

$$2e^2\sum_K \begin{pmatrix}\ell & K & \ell\\ 0 & 0 & 0\end{pmatrix}^2 \frac{[\ell]^2}{[K]}\frac{r_<^K}{r_>^{K+1}}\left(\underset{\sim}{w}_1^{(0K)K}\cdot\underset{\sim}{w}_2^{(0K)K}\right). \tag{37}$$

Only O_β has terms with this angular dependence; the equivalent operator for this interaction, O_{CR}, can therefore be written

$$O_{CR} = \sum_K \beta(0K0KK)\left(\underset{\sim}{w}_1^{(0K)K} \cdot \underset{\sim}{w}_2^{(0K)K}\right). \tag{38}$$

The first nonvanishing term in the expansion of O_{CR} is exactly Eq. (37). The second nonvanishing term is

$$\frac{\mu_0^2}{e^2}\iint\left\{F_1^2F_2^2\ \frac{1}{2}\nabla^2U' - U' \sum_{i\neq j=1,2} F_i^2F_j\left(\frac{d^2}{dr_j^2} - \frac{\ell(\ell+1)}{r_j^2}\right)F_j\right\}\ dr_1dr_2, \tag{39}$$

where $U' = e^2/r_{12}$ and $\nabla^2 = \nabla_1^2 + \nabla_2^2$.

When evaluated in this limit, the matrix element of the term $\sum_i (E^i - \beta_i mc^2)$ contains, in addition to the nonrelativistic energy, a component of the order μ_0^2/e^2. This component is given by

$$\sum_i (\mu_0^2/e^2)(W^i + E_1^i)\left(\frac{d^2}{dr_i^2} - \frac{\ell(\ell+1)}{r_i^2}\right). \tag{40}$$

Combining this expression with Eqs. (36) (summed over i) and (39), one obtains

$$\iint F_1^2F_2^2\left(\frac{1}{2}\nabla^2V - \frac{p^4}{8}\ \frac{1}{m^3c^2}\right)dr_1\ dr_2, \tag{41}$$

where

$$p^4 = (p_1^4 + p_2^4),\ \text{and}\ V = -\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}.$$

To obtain Eq. (41), we have made the approximation that

$$W^i + E^i + \frac{Ze^2}{r_i} - \frac{e^2}{r_{ij}} = \frac{P_i^2}{2m}$$

The first term in Eq. (41) is the Darwin term[8] for two electrons; the second, the mass correction term.

C. Spin Orbit Terms

The spin orbit Hamiltonian can be written as

$$\mathcal{H}_{SO} = - a_{SO} \left[\frac{\ell(\ell+1)(2\ell+1)}{2}\right]^{1/2} \underset{\sim}{w}^{(11)0}, \tag{42}$$

where

$$a_{SO} = \frac{\hbar^2}{2m^2c^2} \frac{1}{r} \frac{dU(r)}{dr}.$$

Because

$$(\underset{\sim}{w}_1^{(11)0} \cdot \underset{\sim}{w}_2^{(00)0}) = (2[\ell])^{-1/2} \underset{\sim}{w}_1^{(11)0},$$

both O_α and O_β contain terms having the angular dependence $\underset{\sim}{w}^{(11)0}$. The relativistic spin orbit constant is then given by

$$a_{SO}^{rel}(i) = - \left[\frac{2}{\ell(\ell+1)(2\ell+1)}\right]^{1/2} \left[\alpha^{i}(110) + (2[\ell])^{-1/2} \beta(11000)\right]$$

$$= \frac{2}{[\ell]} \left[\int (F_+ V_{rel} F_+ + G_+ V_{rel} G_+)_i dr_i - \int (F_- V_{rel} F_- + G_- V_{rel} G_-)_i dr_i\right]. \tag{43}$$

V_{rel} is a "relativistic potential energy" given by

$$V_{rel}(r_1) = - \frac{Ze^2}{r_1} + \frac{e^2}{2[\ell]} \int_0^\infty \left[(2\ell+2)\ (F_+^2 + G_+^2)_2 + 2\ell\ (F_-^2 + G_-^2)_2\right] \frac{1}{r_>} dr_2. \tag{44}$$

where $r_>$ is the larger of r_1, r_2. In the limit discussed above, the second term on the right of (44) becomes the integral over r_2 of the potential energy of a charge at r_1 due to a spherically averaged charged shell at r_2. The relativistic spin orbit term reduces to a_{SO} in the nonrelativistic limit.

D. Orbit-Orbit Terms

The orbit-orbit interaction can be written as[9]

$$\mathcal{H}_{OO} = -16\,\mu_0^2 \sum_K \frac{(2K+1)}{(K+2)} \left\langle \ell \| C^K \| \ell \right\rangle^2 (\ell)(\ell+1)(2\ell+1) \begin{Bmatrix} K & K+1 & 1 \\ \ell & \ell & \ell \end{Bmatrix}^2$$

$$\times \int_0^\infty \int_{r_2}^\infty R_1^2 R_2^2 \frac{r_2^K}{r_1^{K+3}} \, dr_1 \, dr_2 \, (\underset{\sim}{w}_1^{(0K+1)K+1} \cdot \underset{\sim}{w}_2^{(0K+1)K+1}). \tag{45}$$

The equivalent operator for this interaction, O_{OO}, is given by the terms in O_γ and O_δ with the same angular dependence as $\mathcal{H}_{OO}$:

$$O_{OO} = \sum_K \left\{ \gamma(0\,K+1\;0\,K+1\;K+1) + \delta(0\,K+1\;0\,K+1\;K+1) \right\} \left(\underset{\sim}{w}_1^{(0\,K+1)K+1} \cdot \underset{\sim}{w}_2^{(0\,K+1)K+1} \right). \tag{46}$$

Only the terms in this sum with K even will be nonzero. In expanding O_{OO}, one finds that the first nonvanishing term is just $\mathcal{H}_{OO}$.

E. Spin-Other-Orbit Terms

The spin-other-orbit interaction can be written[10]

$$\mathcal{H}_{SOO} =$$

$$2 \sum_K [(K+1)(2\ell+K+2)(2\ell-K)]^{1/2} \Big[(-)^{K+1} [K+1]^{-1/2} (\underset{\sim}{w}^{(0\,K+1)K+1} \cdot \underset{\sim}{w}^{(1\,K)K+1})$$

$$\times \left\{ M^{K-1} \left\langle \ell \| C^{K+1} \| \ell \right\rangle^2 + 2M^K \left\langle \ell \| C^K \| \ell \right\rangle^2 \right\} + (-)^K [K]^{-1/2} (\underset{\sim}{w}^{(0K)K} \cdot \underset{\sim}{w}^{(1\,K+1)K}) \tag{47}$$

$$\times \left\{ M^K \left\langle \ell \| C^K \| \ell \right\rangle^2 + 2M^{K-1} \left\langle \ell \| C^{K+1} \| \ell \right\rangle^2 \right\} \Big] ,$$

where the M^K are the angular integrals of Marvin.[11] The sum over K falls into two parts, the sum over K even and the sum over K odd. For K even, terms in the equivalent operator, O_{SOO}, with the angular dependence $(\underset{\sim}{w}^{(0\,K+1)K+1} \cdot \underset{\sim}{w}^{(1\,K)K+1})$, will arise from O_γ and O_δ; with $(\underset{\sim}{w}^{(0K)K} \cdot \underset{\sim}{w}^{(1\,K+1)K})$, from O_β. For K odd the situation is reversed. The equivalent operator is given by

$$O_{SOO} = \sum_K \Big\{ [\beta(0K\;1\;K{+}1\;K) + \gamma(0K\;1\;K{+}1\;K) + \delta(0\;K\;1\;K{+}1\;K)]\,(\underset{\sim}{w}_1^{(0K)K} \cdot \underset{\sim}{w}_2^{(1\,K+1)K})$$

$$+ [\beta(0\;K{+}1\;1\;K\;K{+}1) + \gamma(0\;K{+}1\;1\;K\;K{+}1) + \delta(0\;K{+}1\;1\;K\;K{+}1)]\,(\underset{\sim}{w}_1^{(0\,K+1)K+1} \cdot \underset{\sim}{w}_2^{(1\,K)K+1}) \Big\} . \qquad (48)$$

The first nonvanishing term in the expansion of Eq. (48) is $\mathcal{H}_{SOO}$.

F. Spin-Spin Terms

The spin-spin Hamiltonian is given by[10]

$$\mathcal{H}_{SS} = 2(5)^{1/2}\ \mu_0^2 \sum_K [(2K+4)\ (2K+3)(2K+2)]^{1/2} \begin{Bmatrix} 1 & 1 & 2 \\ K+2 & K & K+1 \end{Bmatrix} \tag{49}$$

$$\times \langle \ell || C^K || \ell \rangle \langle \ell || C^{K+2} || \ell \rangle \int_0^\infty \int_0^{r_2} R_1^2 R_2^2 \frac{r_1^K}{r_2^{K+3}} dr_1 dr_2 \left(\underset{\sim}{w}_1^{(1\ K+2)} \cdot \underset{\sim}{w}_2^{(1\ K)K+1} \right) .$$

The equivalent operator for this Hamiltonian, O_{SS}, comes from O_γ and O_δ, and is given by

$$O_{SS} = \sum_K \left\{ \gamma(1\ K+2\ 1\ K\ K+1) + \delta(1\ K+2\ 1\ K\ K+1) \right\} \left(\underset{\sim}{w}_1^{(1\ K+2)K+1} \cdot \underset{\sim}{w}_2^{(1\ K)K+1} \right) \tag{50}$$

The only nonzero terms in this sum will occur for K even.

Upon expanding the expression for O_{SS}, we find that the first non-vanishing term is given by Eq. (49) plus the additional term

$$4\mu_0^2 \frac{[(K+1)(K+2)]^{1/2}}{(2K+3)} \langle \ell || C^K || \ell \rangle \langle \ell || C^{K+2} || \ell \rangle$$

$$\int_0^\infty \frac{F_1^4}{r_1^2} dr_1 \left(\underset{\sim}{w}_1^{(1\ K+2)K+1} \cdot \underset{\sim}{w}_2^{(1\ K)K+1} \right) . \tag{51}$$

The radial part of this additional expression is of the form of a delta function between $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$; this term is discussed further in the next section.

G. Spin-Spin Contact Terms

The spin-spin contact Hamiltonian[12] is given by

$$\mathcal{H}_{SSC} = -\frac{32\pi}{3}\mu_0^2 (\underset{\sim}{s}_1 \cdot \underset{\sim}{s}_2)\, \delta(\underset{\sim}{r}_1 - \underset{\sim}{r}_2)$$

$$= \frac{4\mu_0^2}{3r^2}\, \delta(r_1 - r_2) \sum_{K\beta} (-)^{K+\beta} \left\langle \ell \| C^K \| \ell \right\rangle^2 \left(\underset{\sim}{w}^{(1\,K)\beta} \cdot \underset{\sim}{w}^{(1\,K)\beta} \right), \tag{52}$$

where we have used[13]

$$\delta(\underset{\sim}{r}_1 - \underset{\sim}{r}_2) = \delta(r_1 - r_2)\, \frac{1}{4\pi r^2} \sum_K [K] \left(C_1^K \cdot C_2^K \right).$$

Again, the equivalent operator for this interaction O_{SSC} comes from O_γ and O_δ,

$$O_{SSC} = \sum_{K\beta} \{\gamma(1\,K\,1\,K\,\beta) + \delta(1\,K\,1\,K\,\beta)\} \left(\underset{\sim}{w}^{(1\,K)\beta} \cdot \underset{\sim}{w}^{(1\,K)\beta} \right).$$

The only nonzero terms in this expansion occur for K even.

Upon expanding O_{SSC}, we find that the first nonvanishing term is given by $\mathcal{H}_{SSS}$ plus some additional terms whose values depend on β. The additional terms are,

for $\beta = K + 1$,

$$\frac{2K\mu_0^2}{3(2K+3)} \left\langle \ell \| C^K \| \ell \right\rangle^2 \int \frac{F_1^4}{r_1^2}\, dr_1 \left(\underset{\sim}{w}_1^{(1\,K)K+1} \cdot \underset{\sim}{w}_2^{(1\,K)K+1} \right); \tag{53a}$$

for $\beta = K - 1$,

$$\frac{2(K+1)\mu_0^2}{3(2K-1)} \left\langle \ell \| C^K \| \ell \right\rangle^2 \int \frac{F_1^4}{r_1^2}\, dr_1 \left(\underset{\sim}{w}_1^{(1\,K)K-1} \cdot \underset{\sim}{w}_2^{(1\,K)K-1} \right); \tag{53b}$$

and for $\beta = K$,

$$\frac{2}{3}\mu_0^2 \left\langle \ell \| C^K \| \ell \right\rangle^2 \int \frac{F_1^4}{r_1^2}\, dr_1 \left(\underset{\sim}{w}_1^{(1\,K)K} \cdot \underset{\sim}{w}_2^{(1\,K)K} \right). \tag{53c}$$

The additional contributions to the spin-spin Hamiltonian found by expanding the equivalent operators in powers of $(v/c)^2$ (Eqs. 51 and 53) can be included in the Hamiltonian by adding the term

$$\mathcal{H}'_{SSC} = -\frac{16\pi}{3}\mu_0^2\, \delta(\underset{\sim}{r}_1 - \underset{\sim}{r}_2) \left[\underset{\sim}{s}_1 \cdot \underset{\sim}{s}_2 - \frac{3(\underset{\sim}{s}_1 \cdot \underset{\sim}{r})(\underset{\sim}{s}_2 \cdot \underset{\sim}{r})}{r^2} \right]. \tag{54}$$

This operator has not been obtained in previous treatments [5, 14] of the spin-spin interaction because earlier results have depended on the assumed shape of the infinitesimal region in which the electrons overlap. The situation is highly analogous to that which exists with respect to the Fermi contact term[15] in hyperfine structure. Judd[7] has found that $\mathcal{H}'_{SSC}$ can be obtained by use of classical electromagnetic theory if the electron spin moments are replaced by currents, as suggested by Casimir.[16] If one uses this method, the result does not depend on the shape of the infinitesimal volume surrounding one of the electrons. Judd[7] has also obtained $\mathcal{H}'_{SSC}$ by the method of Bethe and Salpeter,[5] assuming that electron 1 is excluded from, and electron 2 confined between, two concentric spheres which collapse, in the limit, to a common radius.

Unfortunately, $\mathcal{H}'_{SSC}$, which can be written as

$$\mathcal{H}'_{SSC} = \frac{4(5)^{1/2}\mu_0^2}{r^2} \sum_{K\delta} (-)^{K+\delta}[K,\delta] \begin{pmatrix} 1 & 1 & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} K & \delta & 2 \\ 0 & 0 & 0 \end{pmatrix} \left((\underset{\sim}{s}_1 \underset{\sim}{s}_2)^2 \; (\underset{\sim}{C}_1^K \underset{\sim}{C}_2^\delta)^2 \right)^0, \tag{55}$$

can be shown to always give zero total contribution to the energy. That is, when the matrix element of $\mathcal{H}'_{SSC}$ is taken between the states $|SL\rangle$ and $|S'L'\rangle$, the sum over K and δ can be performed, producing a result which depends on the product

$$\begin{Bmatrix} 1/2 & 1/2 & 1 \\ 1/2 & 1/2 & 1 \\ S & S' & 2 \end{Bmatrix} \begin{pmatrix} L' & \ell & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & \ell & \ell \\ 0 & 0 & 0 \end{pmatrix} .$$

For this productnot to be trivially zero, $S = S' = 1$, and L, L' must be even ; such a state, however, would violate the Pauli principle. It can also be shown that $\mathcal{H}'_{SSC}$ makes zero contribution when evaluated between wave functions arising from mixed configurations.[7]

H. Other Terms

There are three more distinct operators in O_E which have not been discussed. These are

$$O_1 = \sum_K \beta(1\ K{+}1\ 1\ K{+}1\ K) \left(\underset{\sim}{w}_1^{(1\ K+1)K} \cdot \underset{\sim}{w}_2^{(1\ K+1)K}\right),$$

$$O_2 = \sum_K \beta(1\ K{+}1\ 1\ K{-}1\ K) \left(\underset{\sim}{w}_1^{(1\ K+1)K} \cdot \underset{\sim}{w}_2^{(1\ K-1)K}\right),$$

and

$$O_3 = \sum_K \beta(1\ K{-}1\ 1\ K{-}1\ K) \left(\underset{\sim}{w}_1^{(1\ K-1)K} \cdot \underset{\sim}{w}_2^{(1\ K-1)K}\right).$$

Upon expanding these expressions, we find that none has any nonvanishing terms to order μ_0^4/e^4.

V. DISCUSSION

Table I reviews some of the results of the preceding section. In it, the terms in O_E are classified according to the type of fine-structure interaction produced. In the parts of the spin-spin, spin-other-orbit, and orbit-orbit interactions arising from O_γ and O_δ, the angular dependence of each electron is given by $W^{(\alpha\beta)K}$, where K is odd. As was shown in Sec. IIIC and D, in this case $O_\gamma = O_\delta$. In the nonrelativistic limit, the contributions from O_γ and O_δ to the spin-spin contact terms are also equal; this is not the case in the relativistic limit, however.

As mentioned in Sec. III C, the values of O_E do not depend on the particular type of coupling assumed; this implies that the equations for O_E are valid for any two electrons in a configuration ℓ^n. This in turn implies that the equivalent operator for the configuration ℓ^n can be obtained by replacing the indices 1, 2 in O_E by i, j and performing the sums $\sum_{i=1}^{n} O_\alpha^i$ and $\sum_{i>j} (O_\beta + O_\gamma + O_\delta)$.

Using the operators obtained above and relativistic Hartree-Fock wave functions, then, one can calculate in a straightforward manner the value of a particular fine-structure interaction in the configuration ℓ^n. The evaluation of the angular terms is carried out in the nonrelativistic scheme, where the powerful tensor techniques of Racah[17] can be easily utilized. The methods used to obtain these operators can also be used to obtain operators valid for application to mixed configurations.

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FOOTNOTES AND REFERENCES

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Table I. Terms in O_E classified according to corresponding fine-structure interaction. Numbers in first column are KK as defined in Sec. III A. Numbers in second and third columns are k_1, K_1, k_2, K_2, k as defined in Sec. III B, C, and D.

O_α	O_β	O_γ and O_δ	Interaction
0 0			$-Ze^2/r$
1 1	1 1 0 0 0		spin orbit
	0 K 0 K 0 (K even)		e^2/r_{12}
		1 K 1 K+2 K+1 (K even)	spin-spin
		0 K+1 0 K+1 K+1 (K even)	orbit-orbit
		0 K+1 1 K K+1 (K even)	spin-other-orbit
		0 K 1 K+1 K (K odd)	spin-other-orbit
	0 K 1 K+1 K (K even)		spin-other-orbit
	0 K+1 1 K K+1 (K odd)		spin-other-orbit
		1 K 1 K K+1 (K even)	spin-spin contact
		1 K 1 K K (K even)	spin-spin contact
		1 K 1 K K-1 (K even)	spin-spin contact
	1 K+1 1 K+1 K (K even)		
	1 K+1 1 K-1 K (K even)		
	1 K-1 1 K-1 K (K even)		