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Hyperfine Structure Formulas for LS Coupling

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Formulas for the interval factor A and the quadrupole coupling factor B in the hyperfine structure formula,

$$W=W_J+\tfrac{1}{2}AK+BK(K+1),$$

are derived with Racah's tensor algebra. The results are directly applicable to light atoms ($Z<50$) that show good LS coupling. Data of White and Ritchl for manganese are analyzed, and an approximate value of the nuclear quadrupole moment in Mn^{55} of $Q=1\times10^{-24}$ cm^2 is obtained. This confirms another approximate value of $Q=0.5\times10^{-24}$ cm^2 recently obtained by microwave methods. An error in the calculation carried out by Brown and Tomboulian to evaluate the Q of tantalum is noted. A relation satisfied by X functions is derived, which simplifies their numerical evaluation.

A. GENERAL THEORY

THE interaction between the nucleus and electrons of an atom is usually given by the formula,[1]

$$W_F=W_J+\tfrac{1}{2}AK+BK(K+1), \tag{1}$$

where

$$K=F(F+1)-I(I+1)-J(J+1). \tag{2}$$

The dependence of W_F on F (and, practically, on I also) is given by K and the dependence on electronic quantum numbers is included in A and B. The term with A as coefficient arises from the magnetic dipole interaction between the nucleus and the electrons while the term containing B arises from the electric quadrupole moment interaction. The dependence of A and B on the electronic quantum numbers has been calculated only for special electronic configurations,[2–4] usually by writing out the wave functions explicitly, or by use of Goudsmit's sum rule.[3] We give here expressions for A and B that can be evaluated easily with Racah's tensor algebra.[5] The expressions are directly applicable to atoms showing LS coupling. Since relativistic effects[2,4,6] are largely neglected, the atom considered should not have too great an atomic number (say $Z<50$).

Goudsmit[3] has given the following formula which expresses the J dependence of A for an atom showing LS coupling.

$$A(J)=\lambda(2-g)-\sigma\frac{6\Gamma(2-g)-2(g-1)L(L+1)}{(2L-1)(2L+3)}+\beta(g-1),\quad (J\neq0), \tag{3}$$

where[7]

$$\Gamma=\tfrac{1}{2}\{J(J+1)-L(L+1)-S(S+1)\}, \tag{4}$$

$$g=1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}. \tag{5}$$

Goudsmit's derivation by means of the diagonal-sum rule was too cumbersome to publish; we give a more direct derivation of this in Sec. D. Goudsmit did not define the coefficients λ, σ, and β explicitly in terms of one-electron parameters. The procedure outlined in Sec. D yields the following values of λ, σ, and β in terms of double-barred submatrices and tensor operators defined in II; the necessary submatrices are diagonal in αSL, where α represents the quantum numbers needed to specify the electron state (exclusive of S and L).

$$\lambda=\frac{(\alpha SL\|\sum_i(a_l)_i\mathbf{l}_i\|\alpha SL)}{[L(L+1)(2L+1)]^{\frac{1}{2}}}, \tag{6}$$

$$\sigma=-[(2L-1)(2L+3)]^{\frac{1}{2}}\times\frac{(\alpha SL\|\sum_i(a_l)_i\mathbf{s}_i\mathbf{C}_i^{(2)}\|\alpha SL)}{[S(S+1)(2S+1)L(L+1)(2L+1)]^{\frac{1}{2}}}, \tag{7}$$

$$\beta=\frac{(\alpha SL\|\sum_i(a_s)_i\delta(l_i,0)\mathbf{s}_i\|\alpha SL)}{[S(S+1)(2S+1)]^{\frac{1}{2}}}. \tag{8}$$

In these expressions $\mathbf{s}_i$ and $\mathbf{l}_i$ are the spin and angular momentum respectively of the ith electron and $\mathbf{C}^{(2)}$ is the second degree tensor operator defined by Racah in II, Eq. (46). The one-electron parameters a_s and a_l are defined in agreement with the definitions of Fermi[8] and Goudsmit:[3]

$$a_s=\frac{8\pi}{3}R\alpha^2a_0^3\left(\frac{m_e}{M_P}\right)|\psi(0)|^2g(I), \tag{9}$$

$$a_l=R\alpha^2a_0^3\left(\frac{m_e}{M_P}\right)\left\langle\frac{1}{r_l^3}\right\rangle_{\mathrm{Av}}g(I)\quad(l\neq0). \tag{10}$$

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[1] H. Kopfermann, *Kernmomente* (Akad. Verlag. M.B.H., Leipzig, 1940), referred to as I.

[2] H. B. G. Casimir, Verhandel. Teyler's Tweede Genootschap, Haarlem (1936).

[3] S. Goudsmit, Phys. Rev. **37**, 663 (1931).

[4] G. Breit, Phys. Rev. **38**, 463 (1931); G. Breit and L. A. Wills, Phys. Rev. **44**, 470 (1933).

[5] G. Racah, Phys. Rev. **62**, 438 (1942); **63**, 367 (1943), referred to as II and III respectively.

[6] G. Racah, Z. Physik **71**, 431 (1931); Nuovo cimento **8**, 178 (1931).

[7] Tables of g values have been prepared by C. C. Kiess and W. F. Meggers, J. Research Natl. Bur. Standards **1**, 641 (1928).

[8] E. Fermi, Z. Physik **60**, 320 (1930).

In these relations, R is the Rydberg constant; α is the fine structure constant $(=1/137)$; a_o is the Bohr hydrogen radius; m_e/M_p is the ratio of the electron mass to the proton mass $(=1/1836)$; and $g(I)$ is the nuclear g factor.

In Eq. (9), $\psi(0)$ is the value of the eigenfunction of the s-electron at the nucleus. It is usually evaluated by use of a formula given by Fermi and Segrè.[9] When this evaluation is used, a_s takes on a form similar to that suggested by Goudsmit.[10]

$$a_s=\frac{8}{3}\frac{m_e}{M_P}\frac{\alpha^2}{R^{\frac{1}{2}}}\frac{Z}{Z_0}W^{\frac{3}{2}}g(I)\kappa(\tfrac{1}{2},Z)\left(1-\frac{ds}{dn}\right)$$

$$=2.32\times10^{-10}W^{\frac{3}{2}}\frac{Z}{Z_0}g(I)\kappa(\tfrac{1}{2},Z)\left(1-\frac{ds}{dn}\right).\quad(11)$$

In this expression a_s is measured in kaysers.[11] W is the energy in kaysers needed to remove the s electron from the atom in that stage of ionization in which it is the outer electron; Z is the atomic number; and Z_0 is one for neutral atoms, two for singly ionized atoms, etc. The factor $\kappa(\frac{1}{2}, Z)$ is a relativistic correction[6] tabulated in I. The rate of change of the quantum defect ds/dn can be evaluated if other members of the series are known; neglecting this factor will generally make the calculated value of a_s a little too small.

The value of $\langle 1/r_l^3\rangle_{\text{Av}}$ in Eq. (10) can be related to the spin-orbit parameter ζ_l by the equation

$$\zeta_l=R\alpha^2a_o^3Z_i\langle 1/r_l^3\rangle_{\text{Av}}\lambda(l,Z).\quad(12)$$

Z_i is an effective nuclear charge, about two less than Z for p-electrons and 10 less than Z for d electrons, and $\lambda(l, Z)$ is another relativistic correction[6] which is tabulated in I. The value of ζ_l is determined from an analysis of the experimentally-observed fine structure of the term by methods outlined in Appendix II. By means of Eq. (12), relation (10) takes the form

$$a_l=\frac{m_e}{M_P}\frac{\zeta_l}{\lambda(l,Z)Z_i}g(I)=0.545\frac{\zeta_l}{\lambda(l,Z)Z_i}g(I)\times10^{-3}.\quad(13)$$

Both a_l and ζ_l are measured in kaysers.

The expression usually given for B is that due to Casimir.[2]

$$B=-\frac{3}{8}\frac{e^2Q}{I(2I-1)J(2J-1)}$$

$$\times\left\langle\left\{\sum_i\frac{(3\cos^2\theta_i-1)}{r_i^3}\right\}_{M_J=J}\right\rangle_{\text{Av}}.\quad(14)$$

The electric quadrupole moment Q of the nucleus is defined in Sec. E (it is measured in cm^2); θ_i is the angle which the radius vector r_i of the ith electron makes with the Z axis. The J dependence of B is not shown explicitly in this formula. To express this dependence we have derived in Sec. E the following expression for B:

$$B(J)=\gamma\frac{8\{3(2-g)[J(J+1)(2-g)-\frac{1}{2}]-L(L+1)\}}{(2J-1)(2J+3)(2L-1)(2L+3)},$$

$$(J\neq0,\tfrac{1}{2}).\quad(15)$$

The coefficient γ, which is independent of J, is given by:

$$\gamma=-[(2L-1)(2L+3)]^{\frac{1}{2}}$$

$$\times\frac{(\alpha SL\|\sum_i(b_l)_i\mathbf{C}_i^{(2)}\|\alpha SL)}{[L(L+1)(2L+1)]^{\frac{1}{2}}}.\quad(16)$$

The one-electron parameter is defined as

$$b_l=\frac{3e^2Q}{16I(2I-1)}\langle 1/r_l^3\rangle_{\text{Av}}.\quad(17)$$

By use of (12), since $e^2=2Ra_o$, it can be evaluated as

$$b_l=\frac{3}{8\alpha^2a_o^2}\frac{\zeta_l}{\lambda(l,Z)Z_i}\frac{Q}{I(2I-1)}$$

$$=\frac{0.253\zeta_l}{\lambda(l,Z)Z_i}\frac{Q}{I(2I-1)}\times10^{21},\quad(18)$$

where b_l and ζ_l are in kaysers and Q in units of cm^2. If b_l is measured in millikaysers and Q in units of barns (10^{-24} cm^2), then the factor 10^{21} can be omitted.

For one-electron configurations, the values of A and B have a particularly simple form. Entering the following expressions from II into the general formulas (6), (7), (8), and (16),

$$(l\|\mathbf{l}\|l)=[l(l+1)(2l+1)]^{\frac{1}{2}},\quad(19)$$

$$(\tfrac{1}{2}\|\mathbf{s}\|\tfrac{1}{2})=\sqrt{\tfrac{3}{2}},\quad(20)$$

$$(l\|\mathbf{C}^{(2)}\|l)=-\left[\frac{l(l+1)(2l+1)}{(2l-1)(2l+3)}\right]^{\frac{1}{2}},\quad(21)$$

one finds for the one-electron configurations that $\lambda=\sigma=a_l$, $\beta=a_s$, and $\gamma=b_l$. Entering these values into (3) and (15) we have,

$$A=a_s,\qquad(l=0),\quad(22)$$

$$A(J)=\frac{l(l+1)}{j(j+1)}a_l,\qquad(l\neq0),\quad(23)$$

$$B(J)=\frac{b_l}{j(j+1)},\qquad(j\neq\tfrac{1}{2}).\quad(24)$$

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[9] E. Fermi and E. Segrè, Z. Physik **82**, 729 (1933).

[10] S. Goudsmit, Phys. Rev. **43**, 636 (1933).

[11] "Kayser" is the name adopted by the Joint Commission for Spectroscopy for the unit of wave number, cm^{-1}. It is abbreviated "*K*."

The expressions for A have been given by many authors;[12] $A(l+\frac{1}{2})$ and $A(l-\frac{1}{2})$ are usually denoted by a' and a'' respectively. The expression (24) for B is in agreement with results given by Casimir[2] and Racah.[6]

For a term made up of equivalent electrons we write in the notation of II:

$$\begin{aligned}\textstyle\sum_i (a_l)_i \mathbf{s}_i \mathbf{C}_i^{(2)} &= a_l(l\|\mathbf{C}^{(2)}\|l)\mathbf{V}^{(12)},\\ \textstyle\sum_i (b_l)_i \mathbf{C}_i^{(2)} &= b_l(l\|\mathbf{C}^{(2)}\|l)\mathbf{U}^{(2)}.\end{aligned} \tag{25}$$

Relations (7) and (16) become now

$$\sigma = -a_l(l\|\mathbf{C}^{(2)}\|l)[(2L-1)(2L+3)]^{\frac{1}{2}} \times\frac{(l^n\alpha SL\|\mathbf{V}^{(12)}\|l^n\alpha SL)}{[L(L+1)(2L+1)S(S+1)(2S+1)]^{\frac{1}{2}}} \tag{26}$$

$$\gamma = -b_l(l\|\mathbf{C}^{(2)}\|l)[(2L-1)(2L+3)]^{\frac{1}{2}} \times\frac{(l^n\alpha SL\|\mathbf{U}^{(2)}\|l^n\alpha SL)}{[L(L+1)(2L+1)]^{\frac{1}{2}}}. \tag{27}$$

The double barred submatrices of $\mathbf{V}^{(12)}$ and $\mathbf{U}^{(2)}$ are tabulated in III for configurations made up of equivalent p or d electrons; the double barred submatrix of $\mathbf{C}^{(2)}$ has already been given in (21). Because of a relation analogous to (19), $\lambda = a_l$ for groups of equivalent electrons (this is also true for a group of equivalent electrons plus any number of s electrons).

If configurations of non equivalent electrons are coupled together, A and B are evaluated by straightforward application of the decoupling formulas [relations (44)] of II; the results are omitted here for brevity.

B. QUADRUPOLE MOMENT OF MANGANESE

The data of White and Ritchl[13] has been analyzed in an effort to evaluate the quadrupole moment of manganese (Mn^{55}). The two lines $\lambda 5394(^8P_{7/2}\rightarrow {}^6S_{5/2})$ and $\lambda 4033(^6P_{5/2}\rightarrow {}^6S_{5/2})$ lead to the respective Q values 1.10×10^{-24} cm² and 1.01×10^{-24} cm² and from this we conclude that

$$Q = 1\times 10^{-24}\ \text{cm}^2.$$

This value is probably less accurate than the approximate value,

$$Q = 0.5\times 10^{-24}\ \text{cm}^2,$$

recently obtained by microwave methods,[14] but the two determinations do tend to confirm each other.

The Q given above was determined by least squares from the first three line-component intervals only. Successive intervals are less and less well-defined as the lines get wider, weaker, and more closely spaced, and the reproducibility of measurements becomes poor. White and Ritschl give no estimate of the accuracy of their interval measurements, but the increased difficulty involved in the measurements can be appreciated from inspection of the photometer traces they have given for several of their patterns. In the homologous spectra of technetium—where the generally wider spacing allows for better resolution—a weighting procedure was used with the weights defined by the reproducibility of the measurements of the intervals. In some cases this procedure amounted practically to disregarding all but the first two intervals.

The Q values obtained from three other lines of the spectrum, namely $\lambda 5432$ $(^8P_{5/2}\rightarrow {}^6S_{5/2})$, $\lambda 4030$ $(^6P_{7/2}\rightarrow {}^6S_{5/2})$, and $\lambda 4034$ $(^6P_{3/2}\rightarrow {}^6S_{5/2})$, were disregarded; the Q values for these three lines were -2.6, -0.3, and -2.7×10^{-24} cm², respectively. This procedure is justified on the basis of the sensitivity of the intervals to the effects of the quadrupole moment. A suitable criterion for this sensitivity is the difference between the position of the third of three levels with consecutive F values when predicted from the interval between the first two levels with a Landé rule, and when predicted according to the full formula (1); this difference has the value $4B(F-1)(2F-1)$. The quadrupole moment will be determined most accurately from terms in which this quantity is large compared to the accuracy with which the intervals are measured. If we assume $Q = 10^{-24}$ in Mn, and calculate this difference, we get the values for $^8P_{7/2}$, $^6P_{5/2}$, $^8P_{5/2}$, $^6P_{7/2}$, $^6P_{3/2}$ as 0.0035, 0.0036, -0.0013, -0.0022 and -0.0013 kaysers respectively (in Mn I, $\zeta_d = 250$, $Z_i = 15$, $I = 5/2$). These numbers are indicative of the much stronger effect to be expected in the $^8P_{7/2}$ and $^6P_{5/2}$. In technetium, the Q values obtained from the lines corresponding to those neglected in Mn were also too small. The data in technetium were weighted heavily in favor of the $^8P_{7/2}$ and $^6P_{5/2}$ patterns by making a statistical analysis with weights based on the estimated errors of each Q determination as judged by the variability of the Q values obtained from different observations.

Reliable B values can be obtained most easily from lines in which the splitting of one level is zero. In both Mn and Tc, the analysis neglects possible splitting of the $^6S_{5/2}$ ground level. Theoretically, both A and B are zero for this level if it is a pure $d^5s^2\ {}^6S$, and no splitting of this level has been observed directly. By an indirect procedure, White and Ritschl determined an overall splitting of 0.030 K in this ground level in Mn I. They corrected the intervals of the ^8P and ^6P hfs to account for this nonzero splitting. Though these corrections are two or three times as large as the effects of Q evaluated above, the analysis of these corrected intervals leads to very nearly the same Q values as we obtained above from the direct measurements of the lines. The large splitting found by White and Ritchl in the ^6S ground term of Mn is hard to explain, and their analysis may be in error. However, a moderate Landé splitting of this ground term, especially for the transitions in-

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[12] For notes on the literature and a simple derivation see G. Breit, Phys. Rev. **37**, 51 (1931). See also G. Breit and F. W. Doermann, Phys. Rev. **36**, 1732 (1930).

[13] H. E. White and R. Ritchl, Phys. Rev. **35**, 1146 (1930).

[14] Javan, Silvey, Townes, and Grosse, Phys. Rev. **91**, 222 (1953).

volving large F values in Mn and Tc, would have negligible effect on the Q values.

In manganese the levels ${}^6P_{5/2}$ and ${}^6P_{3/2}$ are only 8.73 K apart so that second-order effects of the magnetic interaction might produce perturbations of the hfs pattern and invalidate the determination of Q given above. The matrix elements of the interaction between hfs levels with the same F value in the two fine structure levels were determined by the methods of Sec. D, and found in all cases to be less than $\frac{1}{6}a_s$ (only effects of the s electron were calculated). As a_s has a value of about 0.14 K in Mn I the maximum perturbation to be expected is less than 0.00006 K, so this effect is too small to influence the results.

Observations on Mn I have also been made by Fisher and Peck.[15] Their measurements on λ5394 (${}^8P_{7/2}\rightarrow{}^6S_{5/2}$) and λ5432 (${}^8P_{5/2}\rightarrow{}^6S_{5/2}$) lead to Q values of 3×10^{-24} and -4×10^{-24} cm^2, respectively. The first of these Q values is probably too large since, if it were correct, we would expect more consistent Q values for all lines considered. The second determination is disregarded because of the previously noted low sensitivity of the measurements to effects of Q.

Fisher and Peck evaluated the coefficients λ and σ experimentally in the $d^6({}^5D)s\ {}^6D$ term of Mn I, obtaining the values $\lambda=0.0094$ and $\sigma<0.0001$. From relations (6) and (7) it follows that $\lambda=a_d$ and $\sigma=-a_d/5$. From relation (13) we expect $a_d=0.011$ ($\zeta_d=250$, $Z_i=15$, $g=1.2$), which is in good agreement with the observed value of λ. On this basis, σ should have the value -0.002. It seems unlikely that σ can be evaluated accurately enough from the observed data to make the disagreement between theory and experiment significant.

C. QUADRUPOLE MOMENT OF TANTALUM

Schmidt[16] has determined Q values of tantalum from the ${}^4F_{3/2}$, ${}^4F_{5/2}$, ${}^4F_{9/2}$, and ${}^4P_{3/2}$ levels of the $5d^36s^2$ configuration of Ta I. These Q values are 6.3, 6, 2, 4.2×10^{-24} cm^2, respectively; from these data he has given the value $Q=6\times10^{-24}$ cm^2 for Ta^{181}. Assuming this value of Q, the values of $4B(F-1)(2F-1)$ for these terms are -0.023, -0.010, -0.012, and -0.053 kaysers, respectively (in Ta I, $\zeta_d=1500$, $Z_i=62$, $I=7/2$ as given by Schmidt), so that effects of Q should be easily observable in all patterns. The lower accuracy of the measurement would justify disregarding the low value of Q obtained from the ${}^4F_{9/2}$. The low value of Q obtained for the ${}^4P_{3/2}$ may be attributed to breakdown of LS-coupling. Our unpublished calculations of the energy levels of Ta I in intermediate coupling show that the purities of the four levels considered above are 0.92, 0.97, 0.91, and 0.70, respectively, which tends to bear out this conclusion. The fact that the observed g value of the ${}^4P_{3/2}$ level is much too small (observed $g=1.524$; theoretical $g=1.733$) also confirms this conclusion.

In the non relativistic limit, formulas (15) and (16) lead to the same values of $\langle\{\sum_i(3\cos^2\theta_i-1)\}_{M_J=J}\rangle_{\text{Av}}$ as Schmidt obtained by writing out the eigenfunctions explicitly. In general, to check values of this quantity (when the sum is over a group of equivalent electrons), B is evaluated with (15) and (16) and then multiplied by $-J(2J-1)/2b_l$.

Brown and Tomboulian[17] have recently obtained the value $Q=5.9\times10^{-24}$ cm^2 for Ta^{181} from observations on the $5d^36s\ {}^5F_1$ level of Ta II. We found by the use of relation (15) that their calculation of the matrix element for this level is in error by a factor of two (in the nonrelativistic limit), so that the observed data actually lead to the unreasonably large value of $Q=11.8\times10^{-24}$ cm^2. It is likely that departures from LS coupling, which may be greater in Ta II than in Ta I, are the cause of the discrepancy with respect to Schmidt's value.[18]

D. MAGNETIC DIPOLE INTERACTION BETWEEN THE NUCLEUS AND AN ELECTRON

The interaction of the nuclear magnetic moment with the spin magnetic moment of an electron is that of two magnetic dipoles, and according to (3, 8)I, it has the form

$$H_{I,s}=-a_l\mathbf{I}\cdot\{\mathbf{s}-3\mathbf{r}\mathbf{r}\cdot\mathbf{s}/r^2\},\quad (l\neq0),\qquad(28)$$

where a_l is defined by (10), $\mathbf{I}$ is the vector representing the total nuclear spin, $\mathbf{s}$ is the electron's spin vector, and $\mathbf{r}$ is the radius vector from the nucleus to the electron. The quantity in { } in (28) is a tensor product of order one; according to relation (40) in Appendix I it is equal to $\sqrt{10}[\mathbf{s}\times\mathbf{C}^{(2)}]^{(1)}$ where $\mathbf{C}^{(2)}$ is the tensor operator introduced in II, Eq. (46). The interaction (28) is the scalar product of two vectors, one in the space of nuclear coordinates, the other in the space of electronic coordinates. We have by Eq. (38) in II and Eq. (36) in II,

$$(\alpha J,I,F|H_{I,s}|\alpha J,I,F)$$
$$=\left\{-\frac{\sqrt{10}(\alpha SLJ\|a_l[\mathbf{s}\times\mathbf{C}^{(2)}]^{(1)}\|\alpha SLJ)}{[J(J+1)(2J+1)]^{\frac{1}{2}}}\right\}\frac{K}{2},\qquad(29)$$

where

$$K=F(F+1)-I(I+1)-J(J+1).$$

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[15] R. A. Fisher and E. R. Peck, Phys. Rev. **55**, 270 (1939). In their notation, $\lambda=a(3d^6)$ and $\sigma=b(3d^6)$.

[16] T. Schmidt, Z. Physik **121**, 63 (1943).

[17] B. M. Brown and D. H. Tomboulian, Phys. Rev. **88**, 1158 (1952).

[18] In commenting on the original manuscript of this paper, G. Racah has pointed out that in jj coupling the level $(d_{\frac{3}{2}})^3s$ with $J=1$ has $\langle\sum_i(3\cos^2\theta_i-1)\rangle_{\text{Av}}=\frac{1}{5}$, which is about three times the value of 12/175 valid for the $d^3s\ {}^5F_1$ in LS coupling. Thus the departures from LS coupling are likely to act in the right direction to explain the result. In another private communication, B. M. Brown has informed us that if the worst possible view of the errors is taken, then the λ3042−λ2702 combinations of Ta II lead to the value $B=-0.77\pm0.12$, so that very little of the discrepancy can be due to experimental error.

Using (43) of Appendix I the expression in { } in (29) becomes

$$-\left[\frac{30(2J+1)}{J(J+1)}\right]^{\frac{1}{2}} X\begin{pmatrix} SLJ \\ SLJ \\ 121 \end{pmatrix} (\alpha SL||a_l\mathbf{s}\mathbf{C}^{(2)}||\alpha SL). \quad (30)$$

The X function in (30) has been evaluated in terms of W functions in relation (50) of Appendix I. When the W functions in (50) are explicitly evaluated with (36)II, and the resulting explicit form of the X function is substituted in (30), an expression equal to the second term on the right of (3) [where σ is defined by (7)] is obtained.

The first and last terms on the right of (3) can be obtained similarly. The first term arises from the interaction of the magnetic moment of the nucleus with the field generated by the electron's orbital motion. By (3, 5)I, this interaction has the form:

$$H_{I,l}=a_l\mathbf{I}\cdot\mathbf{l}, \quad (l\neq 0), \quad (31)$$

where $\mathbf{l}$ is the electron's orbital angular momentum. The interaction giving rise to the last term of (3) is derived from the Dirac equation;[12] it applies only to s electrons. According to Eqs. (3) and (28) of I it has the form:

$$H_{I,s}=a_s\mathbf{I}\cdot\mathbf{s}, \quad (l=0), \quad (32)$$

where a_s is defined in (9). However, it is simpler and more direct to use II, Eq. (38) and II, Eq. (44) in carrying out the derivation of these two terms in (3).

All three magnetic interactions (28), (31), and (32), are scalar products of two vectors and have the form:

$$H_v=a_v\mathbf{I}\cdot\mathbf{V}.$$

The Racah method also enables us to calculate nondiagonal elements of these interactions [as well as the diagonal elements needed in deriving (3)]. By Eq. (38) of II we have, in general,

$$\begin{aligned}(\alpha J, I, F|H_v|\alpha' J', I, F)&\\ &=(-1)^{J+I-F}[I(I+1)(2I+1)]^{\frac{1}{2}}\\ &\quad\cdot(\alpha J||a_v\mathbf{V}||\alpha' J')W(JIJ'I;F1). \quad (33)\end{aligned}$$

When $J=J'$, the W function in (33) is proportional to the quantity K which is defined in (29) [in deriving (29) the explicit form of the W function was used]. The general relation (33) is used in conjunction with (43) of Appendix I, which is needed to evaluate the double-barred submatrix, to calculate nondiagonal matrix elements of the electron-nuclear magnetic interactions. The perturbations due to these nondiagonal matrix elements are sometimes responsible for departures of the hfs intervals from the Landé ratio,[2,19] and the production of forbidden electronic transitions.[20]

E. ELECTRIC QUADRUPOLE INTERACTION BETWEEN THE NUCLEUS AND AN ELECTRON

The quadrupole interaction between the nuclear and electronic charge distributions is given by Eqs. (11) and (1) of I as,

$$H_Q=-e^2\int\int\frac{\rho_k r_k^2\rho_e}{r_e^3}(\tfrac{3}{2}\cos^2\vartheta-\tfrac{1}{2})d\tau_k d\tau_e, \quad (34)$$

where ϑ is the angle between the radius vector r_k of an element $e\rho_k d\tau_k$ of nuclear charge and the electronic radius vector r_e and ρ_k and ρ_e are the nuclear and electronic densities, respectively. By II, Eq. (45) the angular factor in (34) is represented as a scalar product of tensor operators,

$$\tfrac{3}{2}\cos^2\vartheta-\tfrac{1}{2}=\mathbf{C}_e^{(2)}\cdot\mathbf{C}_k^{(2)}, \quad (35)$$

and then by (38)II

$$\begin{aligned}(\alpha_e SLJ, \alpha_k I, F|H_Q|\alpha_e SLJ, \alpha_k I, F)&\\ &=-e^2(-1)^{J+I-F}(\alpha_e SLJ||r_e^{-3}\mathbf{C}_e^{(2)}||\alpha_e SLJ)\\ &\quad\cdot(\alpha_k I||r_k^2\mathbf{C}_k^{(2)}||\alpha_k I)W(JI\,JI;F2). \quad (36)\end{aligned}$$

The quadrupole moment Q of the nucleus is defined as a matrix element over the space of nuclear coordinates, evaluated when I has its largest component in the z direction;[2] i.e.,

$$Q=\langle r_k^2(3\cos^2\theta_k-1)_{M_I=I}\rangle_{\mathrm{Av}}. \quad (37)$$

By utilizing II, Eq. (29), and II, Eq. (17), we put this in the form

$$Q=2\left[\frac{I(2I-1)}{(I+1)(2I+1)(2I+3)}\right]^{\frac{1}{2}}(\alpha_k I||r_k^2\mathbf{C}_k^{(2)}||\alpha_k I). \quad (38)$$

When this is substituted in (36), and the W function is evaluated explicitly with Eq. (36) of II we get:

$$\begin{aligned}(\alpha_e SLJ, \alpha_k I, F|H_Q|\alpha_e SLJ, \alpha_k I, F)&\\ &=\left\{\frac{-3e^2Q}{2I(2I-1)}\left\langle\frac{1}{r_e^3}\right\rangle_{\mathrm{Av}}\left[\frac{(2J-2)!}{(2J+3)!}\right]^{\frac{1}{2}}\right.\\ &\quad\left.\cdot(\alpha_e SLJ||\mathbf{C}_e^{(2)}||\alpha_e SLJ)\right\}\\ &\quad\cdot[K(K+1)-(4/3)I(I+1)J(J+1)], \quad (39)\end{aligned}$$

with K again defined as in (29). The first term in brackets [i.e., $K(K+1)$] contributes the third term on the right to the hfs formula (1); its coefficient, the factor in braces, is therefore equal to $B(J)$. This can also be shown more directly by evaluating the expression for $B(J)$ given in (14) with Eq. (29) of II. The contribution of the second term in brackets of (39) is included in W_J [the first term on the right in (1)].

The J dependence of $B(J)$ is obtained by evaluating the submatrix in the factor in braces in (39) with

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[19] S. Goudsmit and R. F. Bacher, Phys. Rev. **43**, 894 (1933).

[20] S. Mrozowski, Phys. Rev. **67**, 161 (1945); K. G. Kessler, Phys. Rev. **77**, 559 (1950); F. F. Deloume and J. R. Holmes, Phys. Rev. **76**, 174 (1949).

Eq. (44) of II; this leads directly to the formula given in (15) and (16).

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APPENDIX I

An extension of the theory in II is given in Sec. I of this Appendix. This extension is equivalent to results given by G. Racah and U. Fano in unpublished manuscripts.

1. *J* Dependence of an Irreducible Tensor in *LS* Coupling

The interactions encountered in atomic spectroscopy are generally (a) scalars with respect to J, or else (b) they commute with either L or S; Eqs. (38) and (44), respectively, of II are adequate to specify the J dependence of the interactions in such cases. The interactions (31), (32), and (34) are examples of the type (b). However, the interaction (28) behaves as a vector with respect to J and does not commute with either L or S. The following extension of the theory in II allows us to calculate the J dependence in such cases.

A tensor of degree k_1 which is irreducible with respect to S and commutes with L can be combined with a tensor of degree k_2, irreducible with respect to L and commuting with S, to produce a tensor of degree k $(k_1+k_2 \geqslant k \geqslant |k_1-k_2|)$ called the tensor product, which is irreducible with respect to J by use of the relation,[21]

$$\begin{aligned}\mathbf{P}_q^{(k)} &\equiv [\mathbf{T}^{(k_1)}\times\mathbf{U}^{(k_2)}]_q^{(k)}\\ &= \sum_{q_1q_2} \mathbf{T}_{q_1}^{(k_1)}\mathbf{U}_{q_2}^{(k_2)}(k_1q_1k_2q_2|k_1k_2kq). \qquad (40)\end{aligned}$$

To obtain matrix elements of such a tensor between states showing LS coupling, Eqs. (16) and (29) of II are first utilized:

$$\begin{aligned}&(\alpha SLJM|\mathbf{P}_q^{(k)}|\alpha' S'L'J'M')\\ &\quad=(-1)^{J+M+k+q}(2k+1)^{\frac{1}{2}}\sum_{\alpha''J''}(-1)^{J''}\\ &\qquad\cdot(\alpha SLJ\|\mathbf{T}^{(k_1)}\|\alpha'' S'LJ'')\\ &\qquad\cdot(\alpha'' S'LJ''\|\mathbf{U}^{(k_2)}\|\alpha' S'L'J')\\ &\qquad\cdot\Big\{\sum_{q_1q_2M''}(-1)^{M''}V(k_1k_2k;q_1q_2-q)\\ &\qquad\cdot V(JJ''k_1;-MM''q_1)V(J''J'k;-M''M'q_2)\Big\}. \qquad (41)\end{aligned}$$

The sum over the V functions is carried out with (41)II, and then (44)II is used to obtain the result:

$$\begin{aligned}&(\alpha SLJM|\mathbf{P}_q^{(k)}|\alpha' S'L'J'M')\\ &\quad=(-1)^{J+M}V(JJ'k;-MM'q)\\ &\qquad\cdot[(2k+1)(2J+1)(2J'+1)]^{\frac{1}{2}}\\ &\qquad\cdot(\alpha SL\|\mathbf{T}^{(k_1)}\mathbf{U}^{(k_2)}\|\alpha' S'L')\\ &\qquad\cdot\Big\{(-1)^{k-J-J'}\sum_{J''}(2J''+1)W(k_1Jk_2J';J''k)\\ &\qquad\qquad\cdot W(SJS'J'';Lk_1)W(LJ''L'J';S'k_2)\Big\}. \qquad (42)\end{aligned}$$

By comparing this with Eq. (29) of II, and representing the summation in braces as an X function in agreement with the definition of Fano,[22] we put this result in the final form,

$$\begin{aligned}&(\alpha SLJ\|\mathbf{P}^{(k)}\|\alpha' S'L'J')\\ &\quad=(\alpha SL\|\mathbf{T}^{(k_1)}\mathbf{U}^{(k_2)}\|\alpha' S'L')\\ &\qquad\cdot[(2k+1)(2J+1)(2J'+1)]^{\frac{1}{2}}X\begin{pmatrix}SLJ\\ S'L'J'\\ k_1k_2k\end{pmatrix}, \qquad (43)\end{aligned}$$

where

$$\begin{aligned}X\begin{pmatrix}SLJ\\ S'L'J'\\ k_1k_2k\end{pmatrix}&=(-1)^{k-J-J'}\sum_{J''}(2J''+1)\\ &\quad\cdot W(k_1Jk_2J';J''k)W(SJS'J'';Lk_1)\\ &\quad\cdot W(LJ''L'J';S'k_2). \qquad (44)\end{aligned}$$

The following are some miscellaneous properties of the X function. If any of the 9 arguments is zero, the X function reduces to a W function; in particular, if $k=0$ then (43) is equivalent to Eq. (38) of II, while if $k_1=0$ or $k_2=0$ it is equivalent to Eq. (44) of II. The function vanishes if the triangular condition is not satisfied by any of the six triads forming the rows and columns of the function. The function is invariant with respect to interchange of rows and columns. Interchange of two rows or columns multiplies the function by

$$(-1)^{S+L+J+S'+L'+J'+k_1+k_2+k}.$$

As a consequence, when $(SLJ)=(S'L'J')$ the function vanishes unless k_1+k_2+k is even.

2. An Identity Satisfied by *X* Functions

We have derived an identity which can be used to simplify the numerical calculation of the X function. Relation (44) is multiplied on both sides by $(-1)^k(2k+1)W(J'k\beta k_2;Jk_1)$, and a sum over k is carried out on the right by using Eqs. (40) and (43)

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[21] G. Racah, "Group Theory and Spectroscopy," lecture notes, Princeton University, 1951 (unpublished).

[22] U. Fano, Natl. Bur. Standards Rep. No. 1214 (unpublished) 1951.

of II to obtain

$$\sum_k (-1)^k(2k+1)W(J'k\beta k_2;Jk_1)X\left\{\begin{matrix}SLJ\\S'L'J'\\k_1k_2k\end{matrix}\right\}$$
$$=(-1)^{L-\beta-S'-2k_2}\sum_{J''}W(LJ''Sk_1;S'J)$$
$$\cdot W(J'J''\beta J;k_2k_1)W(LJ''L'J';S'k_2). \quad (45)$$

By using the following identity given by Biedenharn:[23]

$$\sum_\lambda (2\lambda+1)W(a'\lambda\alpha c;ac')W(b\lambda\beta c';b'c)W(a'\lambda\gamma b;ab')$$
$$=W(a\alpha b\beta;c\gamma)W(a'\alpha b'\beta;c'\gamma), \quad (46)$$

relation (45) can be reduced to the following form:

$$\sum_k (-1)^k(2k+1)W(J'k\beta k_2;Jk_1)X\left\{\begin{matrix}SLJ\\S'L'J'\\k_1k_2k\end{matrix}\right\}$$
$$=(-1)^{L-\beta-S'-2k_2}W(S'SJ'\beta;k_1L')$$
$$\cdot W(k_2\beta LS;JL'). \quad (47)$$

By making use of the symmetry properties of the X function, summation can be carried out over any other argument (to permit this, no use has been made of the integral nature of any argument in the X function). For instance, to simplify the X function needed in Sec. D we use

$$\sum_{k_2} (-1)^{k_2}(2k_2+1)W(Lk_2\beta k;L'k_1)X\left\{\begin{matrix}SLJ\\S'L'J'\\k_1k_2k\end{matrix}\right\}$$
$$=(-1)^{J'-\beta-S-2k}W(SS'L\beta;k_1J)$$
$$\cdot W(k\beta J'S';L'J). \quad (48)$$

In the case where $k_1=k=1$ and $(S'L'J')=(SLJ)$, the X-function in the sum of (48) with $(k_1k_2k)=(111)$ vanishes as indicated in the last sentence of Sec. 1 of this Appendix. Hence, taking $\beta=L$, relation (48) becomes,

$$W(L1L1;L0)X\left\{\begin{matrix}SLJ\\SLJ\\101\end{matrix}\right\}+5W(L1L1;L2)X\left\{\begin{matrix}SLJ\\SLJ\\121\end{matrix}\right\}$$
$$=W(SLSL;J1)W(LJLJ;S1). \quad (49)$$

Noting that $W(L1L1;L0)=-[3(2L+1)]^{-\frac{1}{2}}$ and that the X-function containing zero reduces to a W function, this finally becomes

$$X\left\{\begin{matrix}SLJ\\SLJ\\121\end{matrix}\right\}=\frac{3(2L+1)W(LSLS;J1)W(LJLJ;S1)-(-)^{L-S-J}W(SJSJ;L1)}{15(2L+1)W(L1L1;L2)}. \quad (50)$$

In general it would require the evaluation of nine W functions for each J value to calculate the X function in (50) directly from the sum in (44); the relation (50) simplifies this so that only three W functions need be evaluated for each J value.

In the calculation of X functions for which $(SLJ)\neq(S'L'J')$, simplification may result from the vanishing of certain X functions in the sum in (48) because of failure of the triangular conditions.

APPENDIX II

In the first-order approximation, the spin-orbit interaction displaces a level by the amount $\zeta(\alpha SL)\Gamma$,[24] where Γ is defined by (4) and where

$$\zeta(\alpha SL)=\frac{(\alpha SL||\sum_i(\zeta_l)_i\mathbf{s}_i\mathbf{l}_i||\alpha SL)}{[S(S+1)(2S+1)L(L+1)(2L+1)]^{\frac{1}{2}}}. \quad (51)$$

In this expression, ζ_l is the radial parameter given in (12) according to the evaluation with a Coulomb field.[24]

For one-electron configurations we have:

$$(l||\mathbf{sl}||l)=[\tfrac{3}{2}l(l+1)(2l+1)]^{\frac{1}{2}}. \quad (52)$$

In this case $\zeta(l)=\zeta_l$ and the doublet separation is

$$E_J-E_{J-1}=J\zeta(\alpha SL)=(l+\tfrac{1}{2})\zeta_l. \quad (53)$$

The doublet separation is sometimes denoted by δ.

In configurations of equivalent electrons

$$\zeta(l^n\alpha SL)=[l(l+1)(2l+1)]^{\frac{1}{2}}$$
$$\cdot\frac{(l^n\alpha SL||\mathbf{V}^{(11)}||l^n\alpha SL)}{[S(S+1)(2S+1)L(L+1)(2L+1)]^{\frac{1}{2}}}\zeta_l. \quad (54)$$

Values of the tensor $\mathbf{V}^{(11)}$ are tabulated in III for p and d electrons.

If nonequivalent electrons are coupled together relations (44) of II are used to calculate $\zeta(\alpha SL)$.

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[23] L. C. Biedenharn, J. Math. Phys. **31**, 287 (1953).

[24] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1951), pp. 194 and 123.