PHYSICAL REVIEW VOLUME 126, NUMBER 5 JUNE 1, 1962

Second-Order Hyperfine and Zeeman Corrections for an (*sl*) Configuration*

A. Lurio
Watson Laboratory, International Business Machines Corporation, New York, New York

M. Mandel
Stanford University, Stanford, California

and

R. Novick†
Columbia University, New York, New York

(Received November 28, 1961)

The complete Zeeman and hyperfine (dipole, quadrupole, and octupole) matrices are given for an (*sl*) configuration in intermediate coupling. From these are derived the second-order corrections to the zero-field hyperfine intervals for an (*sp*) configuration. In addition, we obtain the corrections appropriate to the crossing of certain of the hyperfine Zeeman levels of an (*sp*) ${}^3P_1$ state for atoms with spin-$\frac{1}{2}$ and spin-$\frac{3}{2}$ nuclei.

I. INTRODUCTION

A NUMBER of optical resonance[1] and atomic beam experiments[2] have recently been performed on the (*sp*) ${}^3P$ states of the group II and rare-gas elements, other experiments are in progress,[3] and still others are planned. The precision of these experiments necessitates an evaluation of the second-order hyperfine and Zeeman interactions between states associated with different fine-structure levels. In this paper we present the complete matrices for the magnetic dipole, electric quadrupole, magnetic octupole, and Zeeman operators for a general (*sl*) configuration in intermediate coupling.[4] These matrices are used to compute the second-order dipole and quadrupole corrections to the zero-field hyperfine intervals of the ${}^3P$ and ${}^1P$ states of an (*sp*) configuration. These results are applied in an accompanying paper[5] to the analysis of the hyperfine structure (hfs) of the ${}^3P$ states of Zn^{67} and Mg^{25}. Finally, we discuss, in connection with an accompanying paper,[5] the second-order Zeeman, hyperfine, and cross Zeeman-hyperfine corrections to the level-crossing field appropriate to an (*sp*) ${}^3P_1$ atomic state.

In this work we have followed the relativistic methods of Breit and Wills[6] and Casimir[7] in their formulation of the two-electron hyperfine problem, and the method of Schwartz[8] in the evaluation of the single-particle interaction constants. Relativistic and diamagnetic corrections to the Zeeman effect are not discussed. Wherever possible we have used the same notation as Schwartz.[8]

It is assumed that the wave function representing these states may be written as a product of single-electron wave functions. This ignores configuration interaction which may be important in the heavier elements. Since the general problem of the hfs and Zeeman effect for an *s* election and an electron or hole with arbitrary orbital angular momentum *l* (referred to as an *sl* configuration) is only slightly more difficult than the case of an *sp* configuration, we have analyzed this more general problem. As yet, there are no precision measurements of configurations other than *sp* but we expect, for example, that the hfs of the metastable (6*s*5*d*) ${}^3D$ state of barium will be measured in the near future.

II. WAVE FUNCTIONS AND HAMILTONIANS

The electronic configuration, exclusive of closed subshells, consists of two electrons; electron (1) with $l=0$ and electron (or hole) (2) with $l=$arbitrary. In the absence of hyperfine structure and an external field, the *s* and *l* electrons couple to form four states which we designate with the usual Russell-Saunders (RS) symbols ${}^3L_{l+1}$, ${}^3L_l$, ${}^3L_{l-1}$, ${}^1L_l$. The wave functions representing the states of highest and lowest total angular momenta

---

* Work supported in part by the U. S. Air Force monitored by the Air Force Office of Scientific Research of the Air Research and Development Command.

† Alfred P. Sloan Foundation Fellow.

[1] Von Klaus Böchmann, H. Krüger, and E. Rechnagle, Ann. Physik **20**, 250 (1957); G. S. Bogle, J. N. Dodd, and W. L. McLean, Proc. Phys. Soc. (London) **B70**, 796 (1957); P. L. Sagalyn, A. C. Melissinos, and F. Bitter, Phys. Rev. **109**, 375 (1958); P. Thaddeus and R. Novick, Bull. Am. Phys. Soc. **6**, 74 (1961); M. N. McDermott and R. Novick, *ibid.* **6**, 142 (1961); J. Pebay-Peyroula, J. Brossel, and A. Kastler, Compt. rend. **244**, 57 (1957); **245**, 840 (1957); H. Bucka and H. J. Schlüssler, Ann. Physik **7**, 225 (1961).

[2] G. M. Grosof, P. Buck, W. Lichten, and I. I. Rabi, Phys. Rev. Letters **1**, 214 (1958); M. N. McDermott and W. L. Lichten, Phys. Rev. **119**, 134 (1960); W. Faust, M. N. McDermott, and W. Lichten, *ibid.* **120**, 469 (1960); A. Lurio, Bull. Am. Phys. Soc. **4**, 419 and 429 (1959); A. G. Blachman and A. Lurio, Bull. Am. Phys. Soc. **6**, 74 (1961); A. Lurio and A. G. Blachman, *ibid.* **6**, 142 (1961); W. L. Faust and M. N. McDermott, Phys. Rev. **123**, 198 (1961).

[3] Krypton: W. L. Faust and L. Y. C. Chiu, Columbia University (private communication). $\mathrm{Cd}^{107,109}$: M. N. McDermott, R. Novick, and F. Byron, Columbia University (private communication).

[4] Some preliminary results on *sp* configurations have been reported by R. L. Fork, C. V. Stager, and L. C. Bradley, III, Quarterly Progress Report of the Massachusetts Institute of Technology Research Laboratory of Electronics No. 58, July 15, 1960 (unpublished).

[5] A. Lurio, following paper [Phys. Rev. **126**, 1768 (1962)]; P. Thaddeus, and R. Novick, this issue [Phys. Rev. **126**, 1774 (1962)].

[6] G. Breit and L. A. Wills, Phys. Rev. **44**, 470 (1933).

[7] H. B. G. Casimir, *On the Interaction Between Atomic Nuclei and Electron* (Teylers Tweede Genootschap, Haarlem, Holland, 1936).

[8] C. Schwartz, Phys. Rev. **97**, 380 (1955).

are independent of coupling and can be written as[6,7]

$$\psi({}^3L_{l+1})=\psi({}^3L_{l+1}{}^0)=|(\tfrac{1}{2},l+\tfrac{1}{2})_{l+1}\rangle,$$

and

$$\psi({}^3L_{l-1})=\psi({}^3L_{l-1}{}^0)=|(\tfrac{1}{2},l-\tfrac{1}{2})_{l-1}\rangle,$$

where the superscript (0) indicates a pure RS state and the symbol $|(j_1,j_2)_J\rangle$ indicates a pure (jj) coupled state. The wave functions for the two states of total angular momentum l depend on the coupling. We will need to expand these wave functions in terms of both the pure (jj) and pure RS wave functions:

$$\begin{aligned}\psi({}^3L_l)&=c_1|(\tfrac{1}{2},l+\tfrac{1}{2})_l\rangle+c_2|(\tfrac{1}{2},l-\tfrac{1}{2})_l\rangle\\&=\alpha\psi({}^3L_l{}^0)+\beta\psi({}^1L_l{}^0),\end{aligned}\tag{1a}$$

and

$$\begin{aligned}\psi({}^1L_l)&=c_1'|(\tfrac{1}{2},l+\tfrac{1}{2})_l\rangle+c_2'|(\tfrac{1}{2},l-\tfrac{1}{2})_l\rangle\\&=\alpha'\psi({}^3L_l{}^0)+\beta'\psi({}^1L_l{}^0),\end{aligned}\tag{1b}$$

where orthogonality and normalization require that

$$c_1'=c_2,\quad c_2'=-c_1,\quad \alpha'=-\beta,\quad \beta'=\alpha,\quad c_1{}^2+c_2{}^2=\alpha^2+\beta^2=1.\tag{2}$$

The RS and jj expansion coefficients are related by

$$\begin{aligned}\alpha&=c_1\left(\frac{l}{2l+1}\right)^{\frac{1}{2}}+c_2\left(\frac{l+1}{2l+1}\right)^{\frac{1}{2}},\\\beta&=c_1\left(\frac{l+1}{2l+1}\right)^{\frac{1}{2}}-c_2\left(\frac{l}{2l+1}\right)^{\frac{1}{2}}.\end{aligned}\tag{2a}$$

For pure RS coupling we have

$$\begin{aligned}c_1&=\left(\frac{l}{2l+1}\right)^{\frac{1}{2}},\quad c_2=\left(\frac{l+1}{2l+1}\right)^{\frac{1}{2}},\\\alpha&=1,\qquad \beta=0.\end{aligned}\tag{4}$$

The values of c_1 and c_2 (and α and β) depend on the relative magnitude of the spin-orbit and electrostatic interactions between the two electrons and may be estimated in a number of ways to be discussed in Sec. VI.

The interaction Hamiltonian is given by the sum of two terms: $\mathcal{H}_h$, the hyperfine interaction, and $\mathcal{H}_z$, the Zeeman interaction. Following Schwartz,[8] we write the hyperfine term as

$$\mathcal{H}_h=\textstyle\sum_i\sum_k T_e{}^{(k)}(i)\cdot T_n{}^{(k)}=\sum_k\mathcal{H}^{(k)},$$

where the i summation is over the s and l valence electrons and the tensors $T_e{}^{(k)}$ and $T_n{}^{(k)}$ are defined by Schwartz. The superscript k indicates the multipolarity of the hyperfine interaction; $\mathcal{H}^{(1)}$, $\mathcal{H}^{(2)}$, and $\mathcal{H}^{(3)}$ are the dipole, quadrupole, and octupole Hamiltonians respectively.

The Zeeman term is given by

$$\mathcal{H}_z=\mu_0g_S\mathbf{S}\cdot\mathbf{H}+\mu_0g_L\mathbf{L}\cdot\mathbf{H}+\mu_0g_I\mathbf{I}\cdot\mathbf{H},\tag{5}$$

where μ_0 is the Bohr magneton and $\mathbf{H}$ is the magnetic field.

III. MATRIX ELEMENTS

The matrix elements of the relativistic hyperfine operator $\mathcal{H}_h$ are most readily evaluated in the jj coupling scheme.[9] These elements are diagonal in both F and m. Thus,

$$\langle\gamma IJFm|\mathcal{H}_h|\gamma IJ'Fm\rangle=\textstyle\sum_k(-1)^{I+J+F}\begin{Bmatrix}F&J&I\\k&I&J'\end{Bmatrix}\langle(\tfrac{1}{2}j_2)_J\|\sum_i T_e{}^{(k)}(i)\|(\tfrac{1}{2}j_2')_{J'}\rangle\langle I\|T_n{}^{(k)}\|I\rangle,\tag{6}$$

where the two-electron reduced matrix element is related to the single-particle reduced matrix elements by

$$\begin{aligned}\langle(\tfrac{1}{2},j_2)_J\|\textstyle\sum_i T_e{}^{(k)}(i)\|(\tfrac{1}{2}j_2')_{J'}\rangle=&\,\delta_{1,k}\delta_{j_2,j_2'}(-1)^{\frac{3}{2}+j_2+J'}[(2J+1)(2J'+1)]^{\frac{1}{2}}\begin{Bmatrix}\frac{1}{2}&J&j_2'\\J'&\frac{1}{2}&1\end{Bmatrix}\langle\tfrac{1}{2}0\tfrac{1}{2}\|T_e{}^{(1)}(s)\|\tfrac{1}{2}0\tfrac{1}{2}\rangle\\&+(-1)^{\frac{1}{2}+j_2'+J+k}[(2J+1)(2J'+1)]^{\frac{1}{2}}\begin{Bmatrix}j_2&J&\frac{1}{2}\\J'&j_2'&k\end{Bmatrix}\langle\tfrac{1}{2}lj_2\|T_e{}^{(k)}(l)\|\tfrac{1}{2}lj_2'\rangle.\end{aligned}\tag{7}$$

From Schwartz we have:

(a) Single-electron dipole elements

$$\begin{aligned}&\langle\gamma\tfrac{1}{2}lj\|T_e{}^{(1)}\|\gamma\tfrac{1}{2}lj\rangle=(I/\mu_I)[j(j+1)(2j+1)]^{\frac{1}{2}}a_j\\&\langle\gamma\tfrac{1}{2}l\,l+\tfrac{1}{2}\|T_e{}^{(1)}\|\gamma\tfrac{1}{2}l\,l-\tfrac{1}{2}\rangle=-\langle\gamma\tfrac{1}{2}l\,l-\tfrac{1}{2}\|T_e{}^{(1)}\|\gamma\tfrac{1}{2}l\,l+\tfrac{1}{2}\rangle=\frac{-I}{\mu_I}\frac{\xi}{4}\frac{(2l+1)(2l+3)}{[2l(l+1)(2l+1)]^{\frac{1}{2}}}a_{l+\frac{1}{2}},\\&a_j=-\frac{4e\mu_I\kappa}{Ij(2j+2)}\int_0^\infty r^{-2}fgdr=2\frac{\mu_I}{I}\mu_0\frac{l(l+1)}{j(j+1)}\langle 1/r_3\rangle_{\mathrm{av}}F_j,\\&\kappa=l+1,\quad(j=l+\tfrac{1}{2});\quad\kappa=-l,\quad(j=l-\tfrac{1}{2}).\end{aligned}\tag{8a}$$

---

[9] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957).

(b) Single-electron quadrupole elements (lower sign refers to holes)

$$\langle\gamma\tfrac{1}{2}lj\|T_e^{(2)}\|\gamma\tfrac{1}{2}lj\rangle=\pm\left[\frac{(j+1)(2j+1)(2j+3)}{j(2j-1)}\right]^{\frac{1}{2}}\frac{b_j}{2Q},$$

$$\langle\gamma\tfrac{1}{2}l\;l+\tfrac{1}{2}\|T_e^{(2)}\|\gamma\tfrac{1}{2}l\;l-\tfrac{1}{2}\rangle=-\langle\gamma\tfrac{1}{2}l\;l-\tfrac{1}{2}\|T_e^{(2)}\|\gamma\tfrac{1}{2}l\;l+\tfrac{1}{2}\rangle=\mp\frac{\eta b_{l+\frac{1}{2}}}{Q}\left[\frac{3(2l+3)(2l+2)}{2(2l)(2l+1)(2l-1)}\right]^{\frac{1}{2}},\tag{8b}$$

$$b_j=\frac{eQ(2j-1)}{2j+2}\int_0^\infty r^{-3}(f^2+g^2)dr=\frac{2j-1}{2j+2}eQ\langle 1/r^3\rangle_{\text{av}}R_j.$$

(c) Single-electron octupole elements (see Appendix I for the definition of ζ)

$$\langle\gamma\tfrac{1}{2}lj\|T_e^{(3)}\|\gamma\tfrac{1}{2}lj\rangle=-\frac{c_j}{\Omega}\left[\frac{(2j+4)(2j+3)(2j+2)(2j+1)}{2j(2j-2)(2j-1)}\right]^{\frac{1}{2}},$$

$$\langle\gamma\tfrac{1}{2}l\;l+\tfrac{1}{2}\|T_e^{(3)}\|\gamma\tfrac{1}{2}l\;l-\tfrac{1}{2}\rangle=-\langle\gamma\tfrac{1}{2}l\;l-\tfrac{1}{2}\|T_e^{(3)}\|\gamma\tfrac{1}{2}l\;l+\tfrac{1}{2}\rangle=\frac{(2l+5)\zeta c_{l+\frac{1}{2}}}{2\Omega}\left[\frac{(2l+3)(2l+4)}{3(2l+2)(2l+1)(2l)(2l-1)(2l-2)}\right]^{\frac{1}{2}},\tag{8c}$$

$$c_j=-\Omega\frac{2e\kappa(2j-1)}{(2j+4)(2j+2)}\int_0^\infty r^{-4}fgdr=\Omega\mu_0\frac{8l(l-1)(l+1)(l+2)}{(2j+2)(2j+3)(2j+4)}\langle 1/r^5\rangle_{\text{av}}T_j.$$

The relativity correction factors F_j, R_j, and T_j are discussed in Sec. VI. The quantities ξ, η, and ζ are defined in terms of the ratios of the off-diagonal to diagonal matrix elements for the dipole, quadrupole, and octupole operators respectively. These are discussed in Sec. VI and Appendix I. The equation given in Appendix I for ζ does not apply to p electrons. However, it follows from the conservation of angular momentum that the octupole matrix element connecting single-electron $P_{\frac{1}{2}}$ and $P_{\frac{3}{2}}$ states is zero and therefore ζ vanishes when $l=1$.

By combining Eqs. (6)–(8), we obtain the complete

TABLE I. Magnetic dipole matrix elements for an *sl* configuration in intermediate coupling.

Diagonal dipole matrix elements:

$$\langle I^3L_{l+1}Fm|\mathcal{H}^{(1)}|I^3L_{l+1}Fm\rangle=\frac{K}{2}\left\{\frac{a_s}{2l+2}+\frac{2l+1}{2l+2}a_{l+\frac{1}{2}}\right\}$$

$$\langle I^3L_lFm|\mathcal{H}^{(1)}|I^3L_lFm\rangle=\frac{K}{2}\left\{\left(\frac{c_2^2}{2l}-\frac{c_1^2}{2l+2}\right)a_s+\left(c_1^2\frac{2l+3}{2l+2}-2c_1c_2\frac{2l+3}{[(2l)(2l+2)]^{\frac{1}{2}}}\xi\right)a_{l+\frac{1}{2}}+c_2^2\left(\frac{2l-1}{2l}\right)a_{l-\frac{1}{2}}\right\}$$

$\langle I^1L_lFm|\mathcal{H}^{(1)}|I^1L_lFm\rangle=$above with $c_1\rightarrow c_1'$ and $c_2\rightarrow c_2'$

$$\langle I^3L_{l-1}Fm|\mathcal{H}^{(1)}|I^3L_{l-1}Fm\rangle=\frac{K}{2}\left\{-\frac{a_s}{2l}+\frac{2l+1}{2l}a_{l-\frac{1}{2}}\right\}$$

Off-diagonal dipole matrix elements:

$$\langle I^3L_{l+1}Fm|\mathcal{H}^{(1)}|I^3L_lFm\rangle=\{[(l+1)^2-(F-I)^2][(F+I+1)^2-(l+1)^2]\}^{\frac{1}{2}}\frac{1}{2(2l+2)}\left\{c_1a_s-\left[c_1+c_2\frac{(2l+3)\xi}{2[(2l)(2l+2)]^{\frac{1}{2}}}\right]a_{l+\frac{1}{2}}\right\}$$

$\langle I^3L_{l+1}Fm|\mathcal{H}^{(1)}|I^1L_lFm\rangle=$above with $c_1\rightarrow c_1'$ and $c_2\rightarrow c_2'$

$$\langle I^3L_{l+1}Fm|\mathcal{H}^{(1)}|I^3L_{l-1}Fm\rangle=0$$

$$\langle I^3L_lFm|\mathcal{H}^{(1)}|I^3L_{l-1}Fm\rangle=\{[l^2-(F-I)^2][(F+I+1)^2-l^2]\}^{\frac{1}{2}}\frac{1}{2(2l)}\left\{c_2(a_s-a_{l-\frac{1}{2}})-c_1\frac{2l+3}{2[(2l)(2l+2)]^{\frac{1}{2}}}\xi a_{l+\frac{1}{2}}\right\}$$

$\langle I^1L_lFm|\mathcal{H}^{(1)}|I^3L_{l-1}Fm\rangle=$above with $c_1\rightarrow c_1'$ and $c_2\rightarrow c_2'$

$$\langle I^3L_lFm|\mathcal{H}^{(1)}|I^1L_lFm\rangle=\frac{K}{2}\left\{-c_1c_2\left(\frac{1}{2l+2}+\frac{1}{2l}\right)a_s+\frac{2l+3}{2l+2}\left[c_1c_2+\frac{(c_1^2-c_2^2)\xi}{(2l)[(2l)(2l+2)]^{\frac{1}{2}}}\right]a_{l+\frac{1}{2}}-\left(\frac{2l-1}{2l}\right)c_1c_2a_{l-\frac{1}{2}}\right\}$$

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

TABLE II. Quadrupole matrix elements for an *sl* configuration in intermediate coupling.

Diagonal quadrupole matrix elements:

$$\langle I^3L_{l+1}Fm|\mathcal{H}^{(2)}|I^3L_{l+1}Fm\rangle=\frac{3}{2}\frac{[K(K+1)-\frac{4}{3}(l+1)(l+2)I(I+1)]}{(2I)(2I-1)(2l+2)(2l+1)}b_{l+\frac{1}{2}}$$

$$\langle I^3L_lFm|\mathcal{H}^{(2)}|I^3L_lFm\rangle=\frac{3}{2}\frac{[K(K+1)-\frac{4}{3}l(l+1)I(I+1)]}{(2I)(2I-1)(2l)(2l-1)}\left\{\frac{1}{2l+1}\left[c_1^2\frac{(2l-1)(2l+4)}{(2l+2)}-\frac{12c_1c_2\eta}{[(2l)(2l+2)]^{\frac{1}{2}}}\right]b_{l+\frac{1}{2}}+c_2^2b_{l-\frac{1}{2}}\right\}$$

$\langle I^1L_lFm|\mathcal{H}^{(2)}|I^1L_lFm\rangle=$ above with $c_1\rightarrow c_1'$ and $c_2\rightarrow c_2'$

$$\langle I^3L_{l-1}Fm|\mathcal{H}^{(2)}|I^3L_{l-1}Fm\rangle=\frac{3}{2}\frac{[K(K+1)-\frac{4}{3}l(l-1)I(I+1)]}{(2I)(2I-1)(2l-2)(2l-3)}\left\{\frac{(2l+2)(2l-3)}{(2l)(2l-1)}b_{l-\frac{1}{2}}\right\},$$

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

Off-diagonal quadrupole matrix elements:

$$\langle I^3L_{l+1}Fm|\mathcal{H}^{(2)}|I^3L_lFm\rangle=(-)[F(F+1)-I(I+1)-l(l+2)]\{[(F+I+1)^2-(l+1)^2][(l+1)^2-(F-I)^2]\}^{\frac{1}{2}}$$
$$\times\frac{3}{(2I)(2I-1)(2l)(2l+1)(2l+2)}\left\{c_1+c_2\eta\left(\frac{2l+2}{2l}\right)^{\frac{1}{2}}\right\}b_{l+\frac{1}{2}}$$

$\langle I^3L_{l+1}Fm|\mathcal{H}^{(2)}|I^1L_lFm\rangle=$ above with $c_1\rightarrow c_1'$ and $c_2\rightarrow c_2'$

$$\langle I^3L_{l+1}Fm|\mathcal{H}^{(2)}|I^3L_{l-1}Fm\rangle=\{[I^2-(F-l)^2][(l+1)^2-(F-I)^2][(F+I+1)^2-l^2][(F+l+1)^2-(I+1)^2]\}^{\frac{1}{2}}$$
$$\times\frac{3}{(2I)(2I-1)(2l-1)(2l)(2l+1)}\frac{1}{[(2l)(2l+2)]^{\frac{1}{2}}}\eta b_{l+\frac{1}{2}}$$

$$\langle I^3L_lFm|\mathcal{H}^{(2)}|I^3L_{l-1}Fm\rangle=(-)\frac{3[F(F+1)-I(I+1)-(l+1)(l-1)]}{(2I)(2I-1)(2l-1)(2l)(2l+1)}\{[l^2-(F-I)^2][(F+I+1)^2-l^2]\}^{\frac{1}{2}}$$
$$\times\left\{c_1\frac{2l+3}{[(2l)(2l+2]^{\frac{1}{2}}}\eta b_{l+\frac{1}{2}}+c_2\frac{(2l+1)}{(2l-2)}b_{l-\frac{1}{2}}\right\}$$

$\langle I^1L_lFm|\mathcal{H}^{(2)}|I^3L_{l-1}Fm\rangle=$ above with $c_1\rightarrow c_1'$ and $c_2\rightarrow c_2'$

$$\langle I^1L_lFm|\mathcal{H}^{(2)}|I^3L_lFm\rangle=\frac{3}{2}\frac{[K(K+1)-\frac{4}{3}l(l+1)I(I+1)]}{(2I)(2I-1)(2l)(2l-1)}\left\{\frac{1}{2l+1}\left[c_1c_2\frac{(2l-1)(2l+4)}{(2l+2)}+6(c_1^2-c_2^2)\frac{\eta}{[(2l)(2l+2)]^{\frac{1}{2}}}\right]b_{l+\frac{1}{2}}-c_1c_2b_{l-\frac{1}{2}}\right\}$$

matrix of the hyperfine operators in (jj) coupling. These can be transformed to intermediate coupling by application of the transformations given by Eq. (1). The complete two-electron dipole, quadrupole, and octupole matrices in intermediate coupling are given in Tables I, II, and III, respectively. Some of the octupole matrix elements have been expressed in terms of the Wigner $6j$ symbol,[9]

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix}.$$

Convenient numerical tables of these coefficients are available.[10]

The matrix of $\mathcal{H}_z$ (Zeeman operator) is most easily evaluated in pure RS coupling. It is diagonal in m and S (total spin). In intermediate coupling the total spin is no longer a constant of the motion and matrix elements appear that couple states labeled with different values of S. In pure RS coupling we have[10a] (where the Z axis is taken along the magnetic field $\mathbf{H}$)

$$\langle\gamma I(S'L)J'F'm'|\mathcal{H}_z|\gamma I(SL)JFm\rangle=\delta_{S,S'}\delta_{m,m'}(-)^{F'-m'}\begin{pmatrix} F' & 1 & F \\ -m & 0 & m \end{pmatrix}[(2F'+1)(2F+1)]^{\frac{1}{2}}$$
$$\times\left[\delta_{J,J'}(-)^{I+J+F+1}\begin{Bmatrix} I & F' & J \\ F & I & 1 \end{Bmatrix}\langle I\|\mathcal{H}_{zn}\|I\rangle+(-)^{I+J+F'+1}\begin{Bmatrix} J' & F' & I \\ F & J & 1 \end{Bmatrix}\langle J'\|\mathcal{H}_{ze}\|J\rangle\right],\quad(9)$$

---

[10] M. Rotenberg, R. Bivins, N. Metropolis, and J. Wooten, *The 3-j and 6-j Symbols* (The Technology Press, Cambridge, Massachusetts, 1959).

[10a] *Note added in proof.* The m dependence of the Zeeman matrix element is contained in the Wigner $3j$ symbol,[9,10] $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$.

TABLE III. Octupole matrix elements for an *sl* configuration in intermediate coupling.

Diagonal octupole matrix elements:

$$\langle I^3L_{l+1}Fm|\mathcal{H}^{(3)}|I^3L_{l+1}Fm\rangle=M(I;l+1;F;3)C_{l+\frac{1}{2}}$$

$$\langle I^3L_lFm|\mathcal{H}^{(3)}|I^3L_lFm\rangle=M(I;l;F;3)\left\{\frac{(2l+5)}{(2l+2)(2l+1)}\left[(2l-2)c_1^2-\frac{2c_1c_2\zeta}{[(2l)(2l+2)]^{\frac{1}{2}}}\right]C_{l+\frac{1}{2}}+c_2^2C_{l-\frac{1}{2}}\right\}$$

$\langle I^1L_lFm|\mathcal{H}^{(3)}|I^1L_lFm\rangle=$above with $c_1\rightarrow c_1'$ and $c_2\rightarrow c_2'$

$$\langle I^3L_{l-1}Fm|\mathcal{H}^{(3)}|I^3L_{l-1}Fm\rangle=M(I;l-1;F;3)\frac{(2l+3)(2l-4)}{(2l)(2l-1)}C_{l-\frac{1}{2}}$$

where $M(I;J;F;3)=(-)^{I+J+F}\begin{Bmatrix}F & I & J\\ 3 & J & I\end{Bmatrix}\dfrac{[(2J-3)!(2J+4)!(2I-3)!(2I+4)!]^{\frac{1}{2}}}{(2J)!(2I)!}$

or $M(I;J;F;3)=\dfrac{20}{(2I)(2I-1)(2I-2)(2J)(2J-1)(2J-2)}$

$$\times[K^3+4K^2+\tfrac{4}{5}K\{-3I(I+1)J(J+1)+I(I+1)+J(J+1)+3\}-4I(I+1)J(J+1)]$$

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

Off-diagonal octupole matrix elements

$$\langle I^3L_{l+1}Fm|\mathcal{H}^{(3)}|I^3L_lFm\rangle=(-)^{I+F+l+1}\begin{Bmatrix}F & l+1 & I\\ 3 & I & l\end{Bmatrix}(I\|T_n^{(3)}\|I)\left[\frac{(12)(2l+5)(2l+4)(2l+3)}{(2l+2)(2l+1)(2l)(2l-1)}\right]^{\frac{1}{2}}\left[c_1+\frac{c_2}{12}\frac{2l+5}{[(2l)(2l+2)]^{\frac{1}{2}}}\zeta\right]\frac{C_{l+\frac{1}{2}}}{\Omega}$$

$\langle I^3L_{l+1}Fm|\mathcal{H}^{(3)}|I^1L_lFm\rangle=$above with $c_1\rightarrow c_1'$ and $c_2\rightarrow c_2'$

$$\langle I^3L_{l+1}Fm|\mathcal{H}^{(3)}|I^3L_{l-1}Fm\rangle=(-)^{I+F+l}\begin{Bmatrix}F & l+1 & I\\ 3 & I & l-1\end{Bmatrix}(I\|T_n^{(3)}\|I)\left[\frac{5}{6}\frac{(2l+4)(2l+3)}{(2l+1)(2l-1)(2l-2)}\right]^{\frac{1}{2}}\frac{(2l+5)}{(2l)(2l+2)}\zeta\frac{C_{l+\frac{1}{2}}}{\Omega}$$

$$\langle I^3L_{l-1}Fm|\mathcal{H}^{(3)}|I^3L_lFm\rangle=(-)^{I+F+l}\begin{Bmatrix}F & l-1 & I\\ 3 & I & l\end{Bmatrix}(I\|T_n^{(3)}\|I)\left[\frac{(12)(2l+3)(2l+2)(2l+1)}{(2l)(2l-1)(2l-2)(2l-3)}\right]^{\frac{1}{2}}$$

$$\times\left[c_2\frac{C_{l-\frac{1}{2}}}{\Omega}+\frac{c_1}{12}\frac{(2l+5)(2l+4)(2l-3)}{(2l+2)(2l+1)[(2l)(2l+2)]^{\frac{1}{2}}}\zeta\frac{C_{l+\frac{1}{2}}}{\Omega}\right]$$

$\langle I^3L_{l-1}Fm|\mathcal{H}^{(3)}|I^1L_lFm\rangle=$above with $c_1\rightarrow c_1'$ and $c_2\rightarrow c_2'$

$$\langle I^3L_lFm|\mathcal{H}^{(3)}|I^1L_lFm\rangle=(-)^{I+F+l}\begin{Bmatrix}F & l & I\\ 3 & I & l\end{Bmatrix}(I\|T_n^{(3)}\|I)\left[\frac{(2l+4)(2l+3)}{(2l+2)(2l+1)(2l)(2l-1)(2l-2)}\right]^{\frac{1}{2}}$$

$$\times\left\{(2l+5)\left[-c_1c_2(2l-2)+(c_2^2-c_1^2)\frac{\zeta}{[(2l)(2l+2)]^{\frac{1}{2}}}\right]\frac{C_{l+\frac{1}{2}}}{\Omega}+c_1c_2(2l+1)(2l+2)\frac{C_{l-\frac{1}{2}}}{\Omega}\right\}$$

where $(I\|T_n^{(3)}\|I)=\dfrac{[(2I-3)!(2I+4)!]^{\frac{1}{2}}}{(2I)!}(-\Omega)$

where $\mathcal{H}_{zn}=g_I\mu_0I_zH$ and $\mathcal{H}_{ze}=(g_L\mu_0L_z+g_S\mu_0S_z)H$. The nuclear and electronic reduced matrix elements are given by

$$\langle I\|\mathcal{H}_{zn}\|I\rangle=g_I[I(I+1)(2I+1)]^{\frac{1}{2}}\mu_0H,$$

$$\langle J'\|\mathcal{H}_{ze}\|J\rangle=[(2J+1)(2J'+1)]^{\frac{1}{2}}\mu_0H\left[g_L(-)^{L+S+J'+1}\begin{Bmatrix}L & J' & S\\ J & L & 1\end{Bmatrix}[l(l+1)(2l+1)]^{\frac{1}{2}}\right.$$

$$\left.+g_S(-)^{L+S+J+1}\begin{Bmatrix}S & J' & L\\ J & S & 1\end{Bmatrix}[S(S+1)(2S+1)]^{\frac{1}{2}}\right].\tag{10}$$

TABLE IV. Zeeman matrix elements for an *sl* configuration in intermediate coupling.

Zeeman matrix elements in intermediate coupling

$$\langle I^SL_JFm|\mathcal{H}_Z|I^SL_JFm\rangle=\left[g_J'\frac{F(F+1)+J(J+1)-I(I+1)}{2F(F+1)}+g_I\frac{F(F+1)+I(I+1)-J(J+1)}{2F(F+1)}\right]m\mu_0H$$

$$\langle I^SL_JF-1\ m|\mathcal{H}_Z|I^SL_JFm\rangle=(-)\frac{(g_J'-g_I)\mu_0H}{2F}\left[\frac{[F^2-m^2][(I+J+1)^2-F^2][F^2-(J-I)^2]}{4F^2-1}\right]^{\frac{1}{2}}$$

$$\langle I^1L_lFm|\mathcal{H}_Z|I^3L_lFm\rangle=(-)\alpha\beta\frac{(g_S-g_L)}{l(l+1)}\,\frac{F(F+1)+l(l+1)-I(I+1)}{2F(F+1)}m\mu_0H$$

$$\langle I^1L_lF-1\ m|\mathcal{H}_Z|I^3L_lFm\rangle=\langle I^1L_lFm|\mathcal{H}_Z|I^3L_lF-1\ m\rangle=\alpha\beta\frac{(g_S-g_L)\mu_0H}{l(l+1)2F}\left[\frac{[F^2-m^2][(I+l+1)^2-F^2][F^2-(l-I)^2]}{4F^2-1}\right]^{\frac{1}{2}}$$

$$\frac{1}{\alpha}\langle I^3L_lF'm|\mathcal{H}_Z|I^3L_{l\pm1}Fm\rangle=(-)\frac{1}{\beta}\langle I^1L_lF'm|\mathcal{H}_Z|I^3L_{l\pm1}Fm\rangle=\langle I^3L_l{}^0F'm|\mathcal{H}_Z|I^3L_{l\pm1}{}^0Fm\rangle$$

where $F'=F$, $F\pm1$, and the pure *RS* matrix elements (superscript zero) are given by:

$$\langle I^3L_{J-1}{}^0Fm|\mathcal{H}_Z|I^3L_J{}^0Fm\rangle=\langle I^3L_J{}^0Fm|\mathcal{H}_Z|I^3L_{J-1}{}^0Fm\rangle=\frac{(g_S-g_L)m\mu_0H}{4F(F+1)}\left[\frac{[(I+F+1)^2-J^2][J^2-(I-F)^2][J^2-(l-1)^2][(l+2)^2-J^2]}{J^2(4J^2-1)}\right]^{\frac{1}{2}}$$

$$\langle I^3L_{J-1}{}^0F-1\ m|\mathcal{H}_Z|I^3L_J{}^0Fm\rangle=\langle I^3L_J{}^0Fm|\mathcal{H}_Z|I^3L_{J-1}{}^0F-1\ m\rangle$$

$$=\frac{(g_S-g_L)\mu_0H}{4JF}\left[\frac{(F^2-m^2)[(J+F)^2-(I+1)^2][(J+F)^2-I^2][J^2-(l-1)^2][(l+2)^2-J^2]}{(4F^2-1)(4J^2-1)}\right]^{\frac{1}{2}}$$

$$\langle I^3L_{J-1}{}^0Fm|\mathcal{H}_Z|I^3L_J{}^0F-1\ m\rangle=\langle I^3L_J{}^0F-1\ m|\mathcal{H}_Z|I^3L_{J-1}{}^0Fm\rangle$$

$$=\frac{-(g_S-g_L)\mu_0H}{4JF}\left[\frac{(F^2-m^2)[(I+1)^2-(J-F)^2][I^2-(F-J)^2][J^2-(l-1)^2][(l+2)^2-J^2]}{(4F^2-1)(4J^2-1)}\right]^{\frac{1}{2}}$$

$$g_J'({}^3L_{l+1})=g_J({}^3L_{l+1}{}^0)$$

$$g_J'({}^3L_l)=\alpha^2g_J({}^3L_l{}^0)+\beta^2g_J({}^1L_l{}^0)$$

$$g_J'({}^3L_{l-1})=g_J({}^3L_{l-1}{}^0)$$

$$g_J'({}^1L_l)=\alpha^2g_J({}^1L_l{}^0)+\beta^2g_J({}^3L_l{}^0)$$

$$g_J({}^SL_J{}^0)=g_L\frac{J(J+1)+L(L+1)-S(S+1)}{2J(J+1)}+g_S\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

The Zeeman matrix may be transformed to intermediate coupling by application of the transformation given by Eq. (1). The resulting matrix elements are given in Table IV.

IV. ZERO-FIELD HYPERFINE ENERGIES

The energies of the zero-field hyperfine levels are given by

$$W_F=W_F{}^{(1)}+W_F{}^{(2)},$$

where $W_F{}^{(1)}$ is the first-order energy given by

$$W_F{}^{(1)}=A\frac{K}{2}+B\frac{3[K(K+1)-\frac{4}{3}I(I+1)J(J+1)]}{4I(2I-1)(2J)(2J-1)}+CM(I,J,F,3),\tag{11}$$

where K and $M\ (I,J,F,3)$ are defined in Table III.

The hyperfine interaction constants A, B, and C are as follows. Dipole interaction constants:

$$A({}^3L_{l+1})=\frac{a_s}{2l+2}+\frac{2l+1}{2l+2}a_{l+\frac{1}{2}},$$

$$A({}^3L_{l-1})=-\frac{a_s}{2l}+\frac{2l+1}{2l}a_{l-\frac{1}{2}},$$

$$A({}^3L_l)=a_s\left(\frac{c_2{}^2}{2l}-\frac{c_1{}^2}{2l+2}\right)\tag{12}$$

$$+a_{l+\frac{1}{2}}\left(\frac{2l+3}{2l+2}\right)c_1{}^2+a_{l-\frac{1}{2}}\left(\frac{2l-1}{2l}\right)c_2{}^2$$

$$-2c_1c_2\frac{2l+3}{2l(2l+2)[2l(2l+2)]^{\frac{1}{2}}}\xi a_{l+\frac{1}{2}},$$

TABLE V. Second-order corrections to the zero-field hyperfine intervals for an *sp* configuration in intermediate coupling.

Second order corrections to zero-field hyperfine intervals for an *sp* configuration

$$W_F^{(2)}(^3P_2)=\frac{|\langle ^3P_2|\mathcal{H}|^3P_1\rangle|^2}{E(^3P_2)-E(^3P_1)}+\frac{|\langle ^3P_2|\mathcal{H}|^1P_1\rangle|^2}{E(^3P_2)-E(^1P_1)}+\frac{|\langle ^3P_2|\mathcal{H}|^3P_0\rangle|^2}{E(^3P_2)-E(^3P_0)}$$

$$\begin{aligned}W_F^{(2)}(^3P_2)=&\frac{(F+I+3)(F-I+2)(I-F+2)(F+I-1)}{64}\\&\times\left\{\frac{1}{E(^3P_2)-E(^3P_1)}\left[\left(c_1a_s-c_1a_{\frac{3}{2}}-\frac{5\sqrt{2}}{8}c_2\xi a_{\frac{3}{2}}\right)+\frac{I(I+1)-F(F+1)+3}{2I(2I-1)}(c_1+\sqrt{2}c_2\eta)b_{\frac{3}{2}}\right]^2\right.\\&+\frac{1}{E(^3P_2)-E(^1P_1)}\left[\left(c_2a_s-c_2a_{\frac{3}{2}}+\frac{5\sqrt{2}}{8}c_1\xi a_{\frac{3}{2}}\right)+\frac{I(I+1)-F(F+1)+3}{2I(2I-1)}(c_2-\sqrt{2}c_1\eta)b_{\frac{3}{2}}\right]^2\\&\left.+\frac{1}{E(^3P_2)-E(^3P_0)}\left[\frac{(F+I+2)(F-I+1)(I-F+1)(F+I)}{2}\right]\left[\frac{\eta b_{\frac{3}{2}}}{I(2I-1)}\right]^2\right\}\end{aligned}$$

$$W_F^{(2)}(^3P_1)=\frac{|\langle ^3P_1|\mathcal{H}|^3P_2\rangle|^2}{E(^3P_1)-E(^3P_2)}+\frac{|\langle ^3P_1|\mathcal{H}|^1P_1\rangle|^2}{E(^3P_1)-E(^1P_1)}+\frac{|\langle ^3P_1|\mathcal{H}|^3P_0\rangle|^2}{E(^3P_1)-E(^3P_0)}$$

$$\begin{aligned}W_F^{(2)}(^3P_1)=&\frac{(F+I+3)(F-I+2)(I-F+2)(F+I-1)}{64[E(^3P_1)-E(^3P_2)]}\left[\left(c_1a_s-c_1a_{\frac{3}{2}}-\frac{5\sqrt{2}}{8}c_2\xi a_{\frac{3}{2}}\right)+\frac{I(I+1)-F(F+1)+3}{2I(2I-1)}(c_1+\sqrt{2}c_2\eta)b_{\frac{3}{2}}\right]^2\\&+\frac{1}{64[E(^3P_1)-E(^1P_1)]}\left\{[F(F+1)-I(I+1)-2]\left[c_1c_2(5a_{\frac{3}{2}}-2a_{\frac{1}{2}}-3a_s)+(c_1^2-c_2^2)\frac{5\sqrt{2}\xi}{8}a_{\frac{3}{2}}\right]\right.\\&\left.+\frac{3[F(F+1)-I(I+1)-2][F(F+1)-I(I+1)-1]-8I(I+1)}{2I(2I-1)}[c_1c_2+(c_1^2-c_2^2)\eta\sqrt{2}\xi]b_{\frac{3}{2}}\right\}^2\\&+\frac{(F+I+2)(I+1-F)(F+1-I)(F+I)}{16[E(^3P_1)-E(^3P_0)]}\left\{c_2a_s-c_2a_{\frac{1}{2}}-\frac{5\sqrt{2}\xi a_{\frac{3}{2}}}{8}c_1-\frac{[F(F+1)-I(I+1)]}{4I(2I-1)}5\sqrt{2}c_1\eta b_{\frac{3}{2}}\right\}\end{aligned}$$

$W^{(2)}(^1P_1)$ = same expression as for $W^{(2)}(^3P_1)$ except $c_1\rightarrow c_1'$, $c_2\rightarrow c_2'$ and in energy denominators $E(^3P_1)\rightarrow E(^1P_1)$, $E(^1P_1)\rightarrow E(^3P_1)$

$A(^1L_l)$ = above with c_1' and c_2' in place of c_1 and c_2, respectively.

Quadrupole interaction constants:

$$B(^3L_{l+1})=b_{l+\frac{1}{2}},$$

$$B(^3L_{l-1})=\frac{(2l-3)(2l+2)}{2l(2l-1)}b_{l-\frac{1}{2}},$$

$$B(^3L_l)=\frac{(2l-1)(2l+4)}{(2l+1)(2l+2)}c_1^2b_{l+\frac{1}{2}}+c_2^2b_{l-\frac{1}{2}}-\frac{12c_1c_2\eta}{2l(2l+1)}\left(\frac{2l}{2l+2}\right)^{\frac{1}{2}}b_{l+\frac{1}{2}},\tag{13}$$

$B(^1L_l)$ = above with c_1' and c_2' in place of c_1 and c_2, respectively.

Octupole interaction constants:

$$C(^3L_{l+1})=c_{l+\frac{1}{2}},$$

$$C(^3L_{l-1})=\frac{(2l-4)(2l+3)}{2l(2l-1)}c_{l-\frac{1}{2}},$$

$$C(^3L_l)=c_1^2\frac{(2l-2)(2l+5)}{(2l+1)(2l+2)}c_{l+\frac{1}{2}}+c_2^2c_{l-\frac{1}{2}}-\frac{2c_1c_2(2l+5)\zeta c_{l+\frac{1}{2}}}{(2l+2)(2l+1)[(2l)(2l+2)]^{\frac{1}{2}}},\tag{14}$$

$C(^1L_l)$ = same as above with c_1' and c_2' in place of c_1 and c_2, respectively.

The second-order corrections to the zero-field energies for an *sp* configuration are given in Table V. In evaluating the second-order corrections we have included only the dipole and quadrupole terms. The second-order octupole terms are generally not important; however, if desired, they can be evaluated from the matrix elements given in Table III.

V. CORRECTION TO THE LEVEL-CROSSING FIELD FOR AN $(sp)\,^3P_1$ STATE

The level-crossing method of Colgrove, Franken, Lewis, and Sands[11] provides a precise method for determining the magnetic field at which two atomic energy levels become exactly degenerate (or cross). This method has been applied to the fine-structure levels of the $(sp)\,^3P$ states of helium and the hyperfine levels of the first-excited $(sp)\,^3P_1$ state of mercury and cadmium. Here we will concern ourselves with the latter experiments and evaluate the corrections to the crossing-point field arising from second-order hyperfine and Zeeman interactions between states associated with different fine-structure levels. In evaluating these corrections, it is important to remember that the crossing occurs at a field value such that the Zeeman energy is comparable to the zero-field hyperfine splitting of the $^3P_1$ state. In view of this, it is necessary to resort to an exact diagonalization of the submatrix associated with the $^3P_1$ state. The corrections arising from interactions with the other fine-structure levels are obtained by the method of Van Vleck[12] in which a unitary transformation is made to eliminate, to second order, the matrix elements off-diagonal in J and S. The diagonalization of the transformed submatrix leads to a value for crossing-point field which is correct to second-order in the hyperfine and Zeeman terms off-diagonal in J and S.

The corrections appropriate to the crossing of the $^3P_1$ $(F=\frac{3}{2}, m=\frac{3}{2})$ and the $^3P_1$ $(F=\frac{1}{2}, m=-\frac{1}{2})$ states of $\mathrm{Cd}^{111,113}$ (nuclear spin $\frac{1}{2}$) are obtained by this method in an accompanying paper.[5] It is shown that the crossing occurs when

$$g_J'=\frac{-A'(^3P_1)}{\mu_0H_c}-\frac{g_I}{2}-\frac{(6)^{\frac{1}{2}}}{6}\alpha\left[c_2(a_s-a_{\frac{1}{2}})-c_1\frac{5\sqrt{2}\xi}{8}a_{\frac{3}{2}}\right]\frac{1}{E(^3P_1)-E(^3P_0)}+\frac{\sqrt{3}\alpha}{6}\left[c_1a_s-\left(c_1+c_2\frac{5\sqrt{2}\xi}{8}\right)a_{\frac{3}{2}}\right]\frac{1}{E(^3P_2)-E(^3P_1)}$$
$$+\frac{\alpha^2\mu_0H_c}{24}\left[\frac{8}{E(^3P_1)-E(^3P_0)}+\frac{3\beta^2}{E(^1P_1)-E(^3P_1)}-\frac{1}{E(^3P_2)-E(^3P_1)}\right].\quad(15)$$

Here H_c is the crossing field, $E(^SL_J)$ are the fine-structure energies, and $A'(^3P_1)$ is dipole coupling constant for the $^3P_1$ state *without second-order corrections.* g_J' is the gyromagnetic ratio which would be measured at low fields in the $^3P_1$ state for a zero-spin isotope. The first two terms are given by the Breit-Rabi equation, the next two terms are cross hyperfine-Zeeman corrections, and the last term is the second-order Zeeman correction. The second-order hyperfine corrections have been absorbed into the Breit-Rabi term by employing the experimental "A" value for the $^3P_1$ state rather than the corrected value appropriate to an isolated $^3P_1$ state.

In the case of a spin $\frac{3}{2}$ nucleus the crossing of the $^3P_1$ $(F=\frac{5}{2}, m=\frac{5}{2})$ and the $^3P_1$ $(F=\frac{3}{2}, m=\frac{1}{2})$ states occurs when

$$\frac{2A'(1-\frac{1}{4}b)(1+\frac{1}{2}b)}{g_J'\mu_0H_c}=-(1+\tfrac{1}{4}b)-\frac{1}{2}\frac{g_I}{g_J'}\frac{1-\frac{1}{2}b+\frac{5}{16}b^2}{1+\frac{1}{4}b}$$
$$-\frac{1}{12}\frac{(\alpha\mu_0H_c)^2}{A'}\frac{(1+\frac{1}{4}b)^2}{(1-\frac{1}{4}b)(1+\frac{1}{2}b)}\left(\frac{1}{E(^3P_1)-E(^3P_0)}-\frac{1}{8[E(^3P_2)-E(^3P_1)]}\right)$$
$$+\frac{1}{2\sqrt{6}}\frac{1+\frac{1}{4}b}{1+\frac{1}{2}b}\frac{A_0(\alpha\mu_0H_c)}{A'[E(^3P_1)-E(^3P_0)]}-\frac{1}{4\sqrt{3}}\frac{A_2(\alpha\mu_0H_c)}{A'[E(^3P_2)-E(^3P_1)]}\frac{1-\frac{3}{8}b+\frac{7}{32}b^2}{(1-\frac{1}{4}b)(1+\frac{1}{2}b)}$$
$$+\frac{\sqrt{3}}{8}\frac{B_2(\alpha\mu_0H_c)}{A'[E(^3P_2)-E(^3P_1)]}\frac{1+\frac{1}{4}b+\frac{1}{8}b^2}{(1-\frac{1}{4}b)(1+\frac{1}{2}b)}.\quad(16)$$

Here $b=B'/A'$ where A' and B' are the dipole and quadrupole interaction constants for the $^3P_1$ state *without second-order corrections* (see above). In addition we have

$$A_0=c_2(a_s-a_{\frac{1}{2}})-c_1(5\xi/4\sqrt{2})a_{\frac{3}{2}},$$
$$A_2=c_1a_s-[c_1+c_25\xi/4\sqrt{2}]a_{\frac{3}{2}},\quad(17)$$

and

$$B_2=[c_1+c_2\eta\sqrt{2}]b_{\frac{3}{2}}.$$

In obtaining this result we have neglected the terms arising from the interaction with the $^1P_1$ state. In the case of the group II elements these terms are smaller than the terms arising from the $^3P_2$ and $^3P_0$ state by at

---

[11] F. D. Colgrove, P. A. Franken, R. L. Lewis, and R. H. Sands, Phys. Rev. Letters 3, 420 (1959).

[12] See for example E. C. Kemble, *The Fundamental Principles of Quantum Mechanics with Elementary Applications* (Dover Publications, New York, 1937), pp. 394.

least a factor of 100. The first three terms on the right-hand side of Eq. (16) have been obtained previously by Dodd.[13] (He assumed that $b \ll 1$ in the second and third terms.)

VI. EVALUATION OF CONSTANTS AND NUCLEAR MOMENTS

The theoretical expressions for the hfs of the ^3P and ^1P states may be written in terms of the constants c_1, c_2 (or α,β), a_s, $a_{\frac{1}{2}}$, $a_{\frac{3}{2}}$, $b_{\frac{3}{2}}$, $c_{\frac{3}{2}}$, ξ, η, and ζ. In the case of almost all of the atoms of interest the nuclear magnetic moment and the ^3P state hfs have been determined for at least one stable isotope. This allows one to determine the magnetic moment of a new isotope directly from the observed hfs, at least to within the hfs anomaly. In the case of the quadrupole and octupole moments, however, reliable estimates of all of the above constants and $\langle 1/r^3\rangle_{\text{av}}$ and $\langle 1/r^5\rangle_{\text{av}}$ are required. Unfortunately, there are more constants than experimental parameters and we must rely on theoretical estimates of some of these quantities. Here, we will briefly discuss the various methods for estimating the constants and nuclear moments.

The constants[14] ξ, η, and[15] θ all involve the ratio of radial integrals whose main contribution comes from the neighborhood of the nucleus. Breit and Wills, and Casimir have estimated these constants and the various relativistic corrections for a Dirac electron with zero binding energy in a Coulomb field. Schwartz has reevaluated the same quantities for a Dirac electron with finite binding energy and a shielded Coulomb field. Schwartz[14] concludes that Casimir's estimates for ξ, η, and θ are quite reliable; however, he finds that his previous estimate of the octupole integrals are in serious error. He has also shown that in some cases configuration mixing can cause substantial changes in θ. As yet, no one has estimated the configuration mixing corrections to θ for a general (sp) state.

Reliable estimates of the mixing coefficients (c_1,c_2) or (α,β) are difficult to obtain. Three methods have been used to determine these coefficients. In the first method, the deviation of the $^3P_2$, $^3P_1$, $^3P_0$ separations from the Landé interval rule and the $^3P_1$, $^1P_1$ separation is used to estimate the degree of intermediate coupling. This procedure takes account of the spin-orbit interaction, but neglects spin-spin and other interactions.[16] A more rigorous theory for the case of the alkaline earths has been given by Araki,[17] but in this theory there are many more quantities to be determined than there are experimental results. In the second method the lifetime of the $^3P_1$ state is assumed to be determined completely by mixing of the $^3P_1$ and $^1P_1$ states. That is, the natural decay of the $^3P_1{}^0$ state in the absence of mixing is assumed to be negligible. In terms of the measured lifetimes we have:

$$\frac{\beta^2}{\alpha^2}=\frac{\tau(^1P_1)}{\tau(^3P_1)}\frac{\lambda^3(^3P_1-{}^1S_0)}{\lambda^3(^1P_1-{}^1S_0)}, \tag{18}$$

where $\lambda(^SP_1-{}^1S_0)$ is the wavelength corresponding to the transition from the $^SP_1$ state to the ground state. While this method may be expected to be quite reliable, few of the lifetimes have been determined with the necessary precision. In the third method one makes use of the fact that the Landé g_J factors for the $^1P_1$ and $^3P_1$ states are changed by mixing. Thus, for example, the g_J factor for the $^3P_1$ state is given by[17a]

$$g_J(^3P_1)=\tfrac{3}{2}-\tfrac{1}{2}\beta^2+\alpha^2(\tfrac{1}{2}g_S-1)-\tfrac{1}{2}(m/M)(1+\beta^2)+\Delta g, \tag{19}$$

where Δg is the correction for relativistic, diamagnetic, and configuration interaction effects. In the case of the group II elements the effect of mixing on g_J is only slightly larger than the relativistic and diamagnetic correction, so that a reliable theoretical estimate of Δg_J must be made before the mixing coefficients can be obtained from the measured g_J factor. In the case of the $^3P_1$ state of the rare gases the situation is more favorable since the mixing is much greater.

The single-electron quadrupole interaction constant $b_{\frac{3}{2}}$ can be determined from the measured quadrupole interaction constant in either the $^3P_2$ or $^3P_1$ state. In the case of the $^3P_1$ state c_1, c_2, and η are required to make this reduction. The nuclear quadrupole moment can be obtained from $b_{\frac{3}{2}}$ if we can estimate the relativistic correction factor $R_{\frac{3}{2}}$ and the average value of r^{-3} for the p electron $(\langle 1/r^3\rangle_{\text{av}})$. Tables of $R_{\frac{3}{2}}$ are given by Kopfermann.[18] These are based on the work of Casimir. Schwartz has obtained substantially the same corrections with a more refined method (see above). Estimates of $\langle 1/r^3\rangle_{\text{av}}$ can be made from either the observed fine structure, the magnetic hfs constant for the $p_{\frac{3}{2}}$ electron $(a_{\frac{3}{2}})$, or the well-known formulas[18]

$$\begin{aligned} a_0{}^3\langle 1/r^3\rangle_{\text{av}}&=\frac{Z_iZ_0{}^2}{n^{*3}l(l+\frac{1}{2})(l+1)}.\\ a_0{}^3\langle 1/r^3\rangle_{\text{av}}&=\frac{Z_iZ_0{}^2}{l(l+1)(2l+1)}\frac{1}{Rch}\frac{dE}{dn}. \end{aligned} \tag{20}$$

The hfs method is probably the most reliable, provided that we can determine $a_{\frac{3}{2}}$ from the observed hfs in the

---

[13] J. N. Dodd, Proc. Phys. Soc. (London) **77**, 669 (1961).

[14] C. Schwartz, Phys. Rev. **105**, 173 (1957).

[15] $\theta\equiv\frac{1}{5}a_{\frac{1}{2}}/a_{\frac{3}{2}}$.

[16] Hugh C. Wolfe, Phys. Rev. **41**, 443 (1932).

[17] G. Araki, Proc. Phys.-Math. Soc. Japan **19**, 128 and 592 (1937).

[17a] *Note added in proof*. Here, we have neglected the Hughes-Eckart reduced mass correction [see M. Phillips, Phys. Rev. **76**, 1803 (1949)].

[18] H. Kopfermann, *Nuclear Moments* (Academic Press Inc., New York, 1958), 2nd ed.

${}^3P_2$ and ${}^3P_1$ states. This requires a knowledge of c_1, c_2, ξ, and θ. Quadrupole polarization (Sternheimer) effects are discussed by Schwartz.

The nuclear octupole moment is obtained from the octupole interaction constant ($c_{\frac{3}{2}}$) in the ${}^3P_2$ state provided that we can estimate the average value of r^{-5} for the p electron ($\langle 1/r^5\rangle_{\text{av}}$) and the appropriate relativistic correction. The procedures for doing this are discussed by Schwartz. Before extracting $c_{\frac{3}{2}}$ from the observed hfs intervals in the ${}^3P_2$ state, it is essential to subtract out the pseudo-octupole interaction arising from the cross dipole-quadrupole interactions that exist between the ${}^3P_2$ and ${}^3P_1$ states. These corrections can be obtained from the formulas given in Table V.

APPENDIX I

In Eq. (8c) we have written the l-electron off-diagonal octupole-operator reduced matrix element in terms of the constant ζ and the diagonal reduced matrix element for the $j=l+\frac{1}{2}$ state. This constant ζ is introduced in the same manner as the constants ζ and η and we follow the procedure of Casimir and Schwartz to obtain the ratio of the off-diagonal to the diagonal radial integral of the octupole operator, which is expressed in terms of the constant ζ. From Casimir[7] we have for the radial part of the Dirac wave function for a single electron,

$$f(r)=C[\tfrac{1}{2}xJ_{2\rho+1}(x)-(\rho+\kappa)J_{2\rho}(x)],$$
$$g(r)=C\alpha ZJ_{2\rho}(x), \tag{21}$$
$$x=(8Zr/a_0)^{\frac{1}{2}},\quad \rho=(\kappa^2-\alpha^2Z^2)^{\frac{1}{2}},\quad a_0=\hbar^2/me^2,\quad \alpha=e^2/\hbar c,$$

where C is the normalization constant. With these functions the following radial integrals can be evaluated to yield:

$$\int_0^\infty r^{-4}f'g'dr=-C'^2\frac{h}{2mc}\left(\frac{2Z}{a_0}\right)^4\times\frac{10T}{(2l+3)(2l+2)(2l+1)2l(2l-1)(2l+4)},$$
$$\int_0^\infty r^{-4}(f'g''+f''g')dr=-C'C''\left(\frac{2Z}{a_0}\right)^4\frac{h}{2mc}\frac{15(2l-3)!}{(2l+4)!}4L, \tag{22}$$

where T is given by Schwartz and L is a relativistic correction factor given by

$$L=\frac{(\rho'+\rho''-3)!4!2!(2l+4)}{(\rho'-\rho''+3)!(\rho''-\rho'+3)!(\rho'+\rho''+3)!(2l-3)!}, \tag{23}$$

where the prime refers to $j=l+\frac{1}{2}$ and the double prime refers to $j=l-\frac{1}{2}$.

With these definitions we have for the ratio of the off-diagonal to the diagonal radial integrals:

$$\int_0^\infty r^{-4}(f'g''+f''g')dr\Big/\int_0^\infty r^{-4}f'g'dr=-\frac{C''}{C'}\frac{3}{(l-1)}\frac{L}{T}\equiv-\frac{\zeta}{l-1}. \tag{24}$$

The results given in Eqs. (22), (23), and (24) do not apply to p electrons ($l=1$). In such cases the off-diagonal matrix element is zero (see above).