

Some discussion is necessary concerning the accuracy of our assumed value 2.0 for the percentage of quadrupole radiation. Gerjuoy's calculations using the earlier measurements of the relative intensities of the various forbidden lines had indicated a proportion of about 5 percent. This would give for  $H=3880$  a group of five lines of comparable intensity, as in Fig. 7(b). The observed intensities require a figure definitely lower than this. A consideration of the way in which the intensities of these  $\pi$  components change with the percentage of quadrupole radiation assumed, and of the accuracy of the measured intensities, led us to conclude that the figure could not be altered by more than 0.3 percent without definite disagreement with experiment.<sup>10</sup> There is another possible source of error, however, in the presence of the weak line  $\lambda 7346$ . In the parallel effect this gives a single component which should lie almost symmetrically in the gap between the "groups of five." The gap is not wide enough to see the line as separate, so

<sup>10</sup> This was the limit of error given in our preliminary report of the present work, Phys. Rev. **59**, 915A (1941).

probably it merely increases the observed background in this region. It is difficult to estimate the uncertainty due to this cause, since the relative intensity of the line changes rapidly with the temperature of the source, decreasing at higher temperatures. Measurements on one plate of the  $\sigma$  components at  $H=3025$  gave an intensity relative to  $\lambda 7330$  as high as 7 percent, but it was probably less than this on the plates of the  $\pi$  components. If we decrease the assumed background by this amount, the lines become more nearly equal in intensity, but the estimated percentage of quadrupole is raised by only 0.4 percent. It appears necessary to take this uncertainty into account, and to raise our final estimate and its limit of error to  $2.2 \pm 0.5$  percent. As will be shown in the article by E. Gerjuoy, this result is unexpectedly low. Nevertheless, the internal consistency of our results convinces us that there is no large error involved. Further discussion of our results in connection with the theoretical predictions will be found in Gerjuoy's article.

AUGUST 1, 1941

PHYSICAL REVIEW

VOLUME 60

## Interference in the Zeeman Effect of Forbidden Lines

E. GERJUOY

*Department of Physics, University of California, Berkeley, California*

(Received June 13, 1941)

The Zeeman effect of forbidden lines involving simultaneous electric quadrupole and magnetic dipole radiation will exhibit interference between these two different modes of radiation. The predicted intensity of any Zeeman component includes, in general, a term dependent on the fact that both modes of radiation are possible, as well as the usual transition probabilities for independent electric quadrupole and magnetic dipole radiation. Such additional interference terms appear only in the Zeeman effect and not in total line intensities. Proofs of these assertions and formulas for the Zeeman intensities are developed. The latter are compared with observations of the Zeeman effect of the forbidden lines of the  $6p^2$  configuration of Pb I, by Jenkins and Mrozowski. Good agreement with experiment is obtained only if interference is taken into

account. Their observations on the Zeeman effect correspond to a somewhat smaller value of the quadrupole moment of the transition electron in Pb I than is computed from comparison of total line intensities. Both these values of the quadrupole moment of the transition electron are 100 percent or more smaller than that given by a rough estimate from screening constant data using hydrogenic wave functions and the known positions of the levels to evaluate the effective nuclear charge. In the absence of Hartree wave functions for Pb I, no better estimate seems possible. A brief discussion of the hyperfine structure of forbidden lines is included, in which it is shown that the rules for determining the relative intensities of electric dipole hyperfine multiplets also give the intensity ratios in the hyperfine structure of magnetic dipole lines.

**T**HE forbidden lines resulting from transitions between levels of the  $6p^2$  configuration of Pb I have recently been investigated by

Mrozowski and Jenkins. Mrozowski<sup>1</sup> studied the hyperfine structure and relative intensities of the

<sup>1</sup> S. Mrozowski, Phys. Rev. **58**, 1086 (1940).

lines, while Jenkins and Mrozowski<sup>2</sup> have just completed an investigation of the Zeeman effect, including quantitative intensity measurements and the Zeeman effect of the hyperfine structure. Several of the lines of the  $p^2$  configuration, and in particular the lines  $\lambda 7330$  and  $\lambda 9250$  of Pb I, involve simultaneous electric quadrupole and magnetic dipole radiation, and the Zeeman effect of such lines exhibits a new feature of interest, namely interference between the two different modes of radiation. That is, the predicted intensity of any Zeeman component is not, in general, to be found by simply summing the transition probabilities for independent electric quadrupole and magnetic dipole radiation, but must include a term dependent on the fact that both modes of radiation are possible. It is the primary purpose of this paper to derive the expressions for the intensities of the Zeeman components, and compare them with the actual observations of Jenkins and Mrozowski in Pb I. In addition, we shall briefly discuss several problems raised by Mrozowski in his earlier paper on the hyperfine structure and line intensities.<sup>1</sup>

The transition probability for interference radiation may be found by the usual correspondence theory formalism. If the radiation field is due to the presence of simultaneous magnetic dipole and electric quadrupole moments in an oscillating charge distribution of circular frequency  $\nu$ , then, using the more convenient complex fields, we have at large distances<sup>3</sup>

$$\begin{aligned} \mathbf{E} &= \mathbf{E}_m + \mathbf{E}_q, & \mathbf{H} &= \mathbf{H}_m + \mathbf{H}_q, \\ \mathbf{E}_m &= -\frac{\nu^2}{c^2}(\boldsymbol{\beta} \times \mathbf{M}), & \mathbf{E}_q &= \frac{i\nu^3}{2c^3}\{\mathfrak{N} \cdot \boldsymbol{\beta} - (\boldsymbol{\beta} \cdot \mathfrak{N}) \boldsymbol{\beta}\}, \\ \mathbf{H}_m &= \frac{\nu^2}{c^2}(\boldsymbol{\beta} \times \mathbf{M} \times \boldsymbol{\beta}), & \mathbf{H}_q &= \frac{i\nu^3}{2c^3}\boldsymbol{\beta} \times (\mathfrak{N} \cdot \boldsymbol{\beta}) \end{aligned}$$

with the Poynting vector

$$\mathbf{S} = \frac{c}{16\pi}(\mathbf{E} \times \mathbf{H}^* + \mathbf{E}^* \times \mathbf{H}).$$

$\mathfrak{N}$  and  $\mathbf{M}$  are the electric quadrupole and magnetic dipole moments, respectively,  $\boldsymbol{\beta}$  is the unit

<sup>2</sup> F. A. Jenkins and S. Mrozowski, Phys. Rev. **60**, 225 (1941), this issue.

<sup>3</sup> E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, 1935), p. 90 *et seq.* We shall refer to this book as *TAS*.

vector in the direction of propagation. We have omitted the usual  $1/r$  dependence of the field intensities so that  $\mathbf{S}$  gives the average radiation into a solid angle  $d\Omega$  in the direction  $\boldsymbol{\beta}$ . The terms in which we are interested are the cross terms due to the presence of both moments, the other terms give the usual magnetic dipole and electric quadrupole radiation fields. That is, we evaluate that part of the Poynting vector which is

$$\mathbf{R} = \frac{c}{16\pi}(\mathbf{E}_q \times \mathbf{H}_m^* + \mathbf{E}_m \times \mathbf{H}_q^* + \mathbf{E}_q^* \times \mathbf{H}_m + \mathbf{E}_m^* \times \mathbf{H}_q).$$

On dividing the magnitude of  $\mathbf{R}$  by  $\hbar\nu$  ( $\mathbf{R}$  is, of course, a vector in the direction of  $\boldsymbol{\beta}$ ) and substituting twice the proper matrix element for the classical moment we then find the transition probability  $A_i(A, B)$  for the interference radiation into the solid angle  $d\Omega$  in the direction  $\boldsymbol{\beta}$  as the result of a transition between the levels  $A, B$ . By introducing the notation

$$(\gamma JM | \mathfrak{N} | \gamma' J' M') = e\mathbf{Q},$$

$$(\gamma JM | \mathbf{M} | \gamma' J' M')$$

$$= \frac{e\hbar}{2mc}(\gamma JM | \mathbf{L} + 2\mathbf{S} | \gamma' J' M') = \frac{e\hbar}{2mc}\mathbf{D},$$

$$\mathbf{Q} = \mathbf{Q}_1 + i\mathbf{Q}_2, \quad \mathbf{D} = \mathbf{D}_1 + i\mathbf{D}_2,$$

where  $\mathbf{D}$  is measured in units of  $\hbar$ ,  $\mathbf{Q}$  in units of  $a^2$ ,  $a$  the Bohr radius, we find the transition probability  $A_i(A, B)$  between two levels defined by the quantum numbers  $\gamma JM$  and  $\gamma' J' M'$  will be:

$$A_i(\gamma JM, \gamma' J' M') = \frac{\alpha^5 \tau^{-1} \sigma^4}{64\pi} \{ (\boldsymbol{\beta} \cdot \mathbf{Q}_1) \cdot (\mathbf{D}_2 \times \boldsymbol{\beta}) - (\boldsymbol{\beta} \cdot \mathbf{Q}_2) \cdot (\mathbf{D}_1 \times \boldsymbol{\beta}) \} d\Omega. \quad (1)$$

Here  $\sigma$  the wave number is measured in terms of the Rydberg constant,  $\alpha$  is the fine-structure constant, and  $\tau$  is the so-called Hartree unit of time,  $\tau = \hbar^3 m^{-1} e^{-4}$ .

The expression (1) can actually be obtained with less computation from the quantum-mechanical formula for spontaneous emission (which furnishes a check of the correspondence principle method) but the development given here will probably be more familiar to most readers. The quantum-mechanical formulas also

give most readily the probabilities of emission of quanta polarized along an arbitrary direction. It is convenient to have these probabilities and we shall write them down; they may be derived with a little more trouble by the correspondence methods. The transition probabilities for the emission of a quantum in the direction  $\beta$  with the electric vector polarized along  $\omega$  for the quadrupole, dipole, and interference radiations, turn out to be

$$\begin{aligned} A_q^\omega(A, B) &= \frac{1}{4} \frac{\alpha^5 \tau^{-1} \sigma^5}{64\pi} \{ (\beta \cdot \mathbf{Q}_1 \cdot \omega)^2 \\ &\quad + (\beta \cdot \mathbf{Q}_2 \cdot \omega)^2 \} d\Omega, \\ A_m^\omega(A, B) &= \frac{\alpha^5 \tau^{-1} \sigma^3}{64\pi} \{ (\mathbf{D}_1 \times \beta \cdot \omega)^2 \\ &\quad + (\mathbf{D}_2 \times \beta \cdot \omega)^2 \} d\Omega, \\ A_i^\omega(A, B) &= \frac{\alpha^5 \tau^{-1} \sigma^4}{64\pi} \{ (\beta \cdot \mathbf{Q}_1 \cdot \omega)(\mathbf{D}_2 \times \beta \cdot \omega) \\ &\quad - (\beta \cdot \mathbf{Q}_2 \cdot \omega)(\mathbf{D}_1 \times \beta \cdot \omega) \} d\Omega. \end{aligned} \quad (2)$$

That is,  $A_q(A, B)$  and  $A_m(A, B)$  are simply the usual transition probabilities for the emission of electric quadrupole and magnetic dipole radiation, respectively, and the actual intensity of any Zeeman component will be the sum  $A_q + A_m + A_i$ . To evaluate explicitly for any transition we must insert in (2) the actual values of  $\mathbf{D}_1$ ,  $\mathbf{D}_2$ ,  $\mathbf{Q}_1$ ,  $\mathbf{Q}_2$ , which are matrix elements and depend on the quantum numbers of the levels between which the transition is taking place. For convenience in writing formulas, we are not indicating the explicit dependence of  $\mathbf{D}$  and  $\mathbf{Q}$ , which must, however, be kept in mind. The vectorial character of  $\mathbf{D}$  and the dyadic character of  $\mathbf{Q}$  depends only on the change in magnetic quantum number for the particular transition in question.

$$\begin{aligned} \Delta M = 0 \quad \mathbf{D} &= \mathbf{D}_1 + i\mathbf{D}_2 = d(0)\mathbf{k} \\ \mathbf{Q} &= \mathbf{Q}_1 + i\mathbf{Q}_2 = q(0) \left(\frac{2}{3}\right)^{\frac{1}{2}} (\mathbf{k}\mathbf{k} - \frac{1}{2}\mathbf{i}\mathbf{i} - \frac{1}{2}\mathbf{j}\mathbf{j}), \\ \Delta M = \pm 1 \quad \mathbf{D} &= \frac{1}{\sqrt{2}} d(\pm 1) (i \pm ij) \\ \mathbf{Q} &= q(\pm 1) \frac{1}{2} [\mathbf{k}\mathbf{i} + \mathbf{i}\mathbf{k} \pm i(\mathbf{k}\mathbf{j} + \mathbf{j}\mathbf{k})], \\ \Delta M = \pm 2 \quad \mathbf{D} &= 0 \\ \mathbf{Q} &= q(\pm 2) \frac{1}{2} [\mathbf{i}\mathbf{i} - \mathbf{j}\mathbf{j} \pm i(\mathbf{i}\mathbf{j} + \mathbf{j}\mathbf{i})]. \end{aligned}$$

The  $q$ 's and  $d$ 's are readily expressible in terms of the notation of *TAS*.<sup>4</sup> For any pair of levels the  $q$ 's or  $d$ 's are products  $\chi(J)\theta(M, J)$ , the second factor giving the usual  $M$  dependence and the  $\chi(J)$  the appropriate  $D, E, F$  for quadrupole, or  $(\gamma J; M; \gamma' J')$  for magnetic dipole, in the notation of *TAS*, with, of course, the necessary factors to take care of the change in units. Thus, for example, for a transition  $(\gamma JM)$  to  $(\gamma' J - 1M \pm 1)$

$$eq(\pm 1) = \frac{1}{2} E(J \pm 2M + 1) [(J \mp M)(J \mp M - 1)]^{\frac{1}{2}}.$$

We now immediately obtain the transition probabilities for the three modes of radiation for the separate Zeeman components.  $\beta_3$  is the component of  $\beta$  along the magnetic field, which is parallel to the  $z$  axis.

Magnetic dipole:

$$\begin{aligned} \Delta M = 0 \quad A_m(A, B) &= \frac{3}{8\pi} \sigma^3 T_0 d(0)^2 (1 - \beta_3^2) d\Omega, \\ \Delta M = \pm 1 \quad A_m(A, B) &= \frac{3}{16\pi} \sigma^3 T_0 d(\pm 1)^2 (1 + \beta_3^2) d\Omega. \end{aligned}$$

Electric quadrupole

$$\begin{aligned} \Delta M = 0 \quad A_q(A, B) &= \frac{9}{64\pi} \sigma^5 T_0 q(0)^2 (1 - \beta_3^2) \beta_3^2 d\Omega, \\ \Delta M = \pm 1 \quad A_q(A, B) &= \frac{3}{128\pi} \sigma^5 T_0 q(\pm 1)^2 \\ &\quad \times (1 - 3\beta_3^2 + 4\beta_3^4) d\Omega, \\ \Delta M = \pm 2 \quad A_q(A, B) &= \frac{3}{128\pi} \sigma^5 T_0 q(\pm 2)^2 \\ &\quad \times (1 - \beta_3^2)(1 + \beta_3^2) d\Omega. \end{aligned} \quad (3)$$

Interference:

$$\begin{aligned} \Delta M = 0, \pm 2 \quad A_i(A, B) &= 0, \\ \Delta M = \pm 1 \quad A_i(A, B) &= \pm \frac{3}{16\pi} \frac{\sigma^4}{\sqrt{2}} T_0 d(\pm 1) \\ &\quad \times q(\pm 1) (3\beta_3^2 - 1) d\Omega, \\ T_0 &= \alpha^5 \tau^{-1} / 24. \end{aligned}$$

The  $d$ 's and  $q$ 's are not necessarily real quantities, but will actually be real for all spectro-

<sup>4</sup> pp. 63 and 95.

scopic applications. This is because the form of the atomic Hamiltonian is such that the radial eigenfunctions and off-diagonal elements of the central field approximation are real (with the proper choice of phases, of course, but the formulas are always independent of relative phases of the eigenfunctions), and, therefore, the only possible imaginary parts come from the angle integrations, which have been taken into account. For this reason we have not bothered to put absolute value signs into the formulas (3). The vanishing of the interference term for  $\Delta M=0$  is not however contingent on  $\mathbf{D}_2$  and  $\mathbf{Q}_2$  being zero in (1), but is simply due to the fact that  $\boldsymbol{\beta} \cdot \mathbf{Q}$  is a vector in the plane of  $\boldsymbol{\beta}$  and  $\mathbf{k}$  and therefore perpendicular to  $\mathbf{D} \times \boldsymbol{\beta}$ . From (2) we readily discover that for  $\Delta M=0$  the quadrupole radiation is always plane polarized with its electric vector in the plane of  $\boldsymbol{\beta}$  and the magnetic field, whereas the magnetic dipole radiation is polarized perpendicular to that plane. The vanishing of the interference terms for these transitions is thus simply an expression of the fact that radiations polarized in perpendicular planes will not interfere.

Similarly, in the direction of observation perpendicular to the magnetic field, where the interfering components  $\Delta M = \pm 1$  are plane polarized, they are polarized in the same plane, namely with the electric vector parallel to the magnetic field.

By inserting the  $M$  dependence of  $d(\pm 1)$  and  $q(\pm 1)$  in (3) and summing over all  $M, M'$ , for the separate cases  $J-J'=0, \pm 1, \pm 2$ , it is possible to prove directly, though rather tediously, that the sum of the interference terms over all Zeeman components will be zero in any direction, thereby justifying the addition of  $A_m$  and  $A_q$  for ordinary line intensities. In other words the interference can only be observed in the Zeeman effect, the intensity of any line as a whole will simply be the sum of the separately computed magnetic dipole and electric quadrupole intensities. This conclusion is again valid for complex  $d$ 's and  $q$ 's which merely insert absolute value signs and the cosine of a phase difference in (3). We may, however, note more simply that the integral of  $(3\beta_3^2 - 1)$  over all angles is zero. The interference term does not change the total transition probability between any two levels, it merely changes the angular

distribution of the radiation. The total radiation, summed over  $M$  and  $M'$ , must, of course, be spherically symmetric, and the independent electric quadrupole and magnetic dipole terms are also spherically symmetric when summed over  $M$  and  $M'$ . Therefore, it follows that the sum of the interference terms over all Zeeman components must be zero in any direction, since the sum must be the same over all directions by the requirement of spherical symmetry, and the integrated intensity of any interference term over all angles is zero. The way in which the vanishing of the integral of the interference term over all angles comes about can be readily seen from (2).  $\mathbf{Q}$  is a symmetric dyad and  $\mathbf{D}$  a vector. The interchange of  $\boldsymbol{\beta}$  and  $\boldsymbol{\omega}$  in (2) changes the sign of  $A_i^{\omega}(A, B)$ . The contributions from directions with interchanged polarization and propagation vectors cancel out.

Without any desire to belabor the point we may mention that, from the general expansion of the radiation into multipole orders, it can be shown quite generally that the line strengths from different multipoles will not interfere, but for low multipole orders such as quadrupole and dipole, the elementary methods of this paper are much simpler. In conclusion, the intensities at any angle are most conveniently found from (3) by re-expressing the  $d$ 's and  $q$ 's in terms of the line strengths. We shall do this for Pb I. The sign of the interference term in the  $\Delta M = \pm 1$  transitions is, of course, crucial. The correct sign will, however, follow naturally from our formulas; and rules for determining the sign have been stated concisely by Shortley and his collaborators.<sup>5</sup>

#### COMPARISON WITH EXPERIMENT IN Pb I

The  $6p^2$  configuration and some of the data for Pb I as given by Mrozowski<sup>1</sup> are summarized

<sup>5</sup> These conclusions on the Zeeman effect of mixed lines have been arrived at independently by G. H. Shortley, L. H. Aller, J. G. Baker, and D. H. Menzel, *Astrophys. J.*, **93**, 178 (1941), in connection with their tabulations of the strengths of forbidden lines as a function of coupling. They start from the Dirac radiation theory and give the relative intensities at arbitrary angle with the magnetic field of the  $\pi$  and  $\sigma$  components of those Zeeman lines showing interference. These expressions can be readily obtained from our formulas (2). As the only experiments, in Pb I, have been carried out perpendicular to the magnetic field, where the polarizations are plane, it has been sufficient for our purposes to give only the formulas (3) which are nothing more than (2) summed over the two independent directions of polarization.

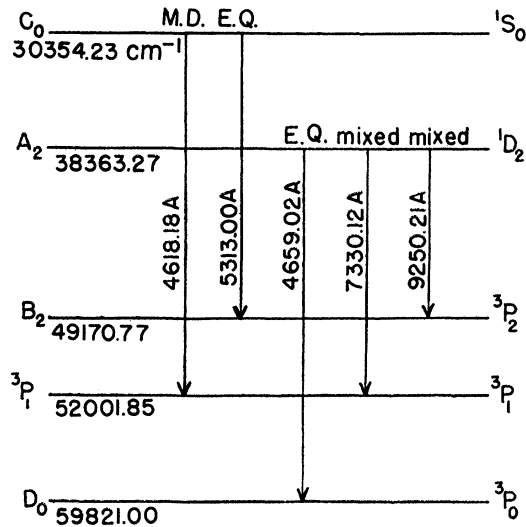


FIG. 1. The lowest levels of Pb I all belonging to the  $6s^26p^2$  configuration. Arrows show the transitions giving the forbidden lines investigated. M.D. = magnetic dipole, E. Q. = electric quadrupole.

in Fig. 1. In the past year several papers have appeared giving general formulas and methods for the calculation of the intensities of forbidden lines in intermediate coupling.<sup>6</sup> It will therefore be sufficient merely to write down the formulas for the line intensities. The line strengths, quadrupole:

$$\begin{aligned}
 S_q(A_2 \ ^3P_1) &= \frac{9}{1} \frac{1}{5} b^2 s_2^2, \\
 S_q(A_2 B_2) &= \frac{6}{3} \frac{1}{5} a^2 b^2 s_2^2, \\
 S_q(A_2 D_0) &= \frac{1}{6} \frac{1}{5} (ad + \frac{1}{2} bc)^2 s_2^2, \\
 S_q(B_2 D_0) &= \frac{1}{6} \frac{1}{5} (bd - \frac{1}{2} ac)^2 s_2^2, \\
 S_q(C_0 B_2) &= \frac{1}{6} \frac{1}{5} (bc + \frac{1}{2} ad)^2 s_2^2,
 \end{aligned} \quad (4)$$

magnetic dipole:

$$\begin{aligned}
 S_m(A_2 \ ^3P_1) &= \frac{5}{2} b^2, \\
 S_m(A_2 B_2) &= \frac{1}{5} \frac{1}{2} a^2 b^2, \\
 S_m(C_0 \ ^3P_1) &= 2d^2.
 \end{aligned}$$

The lines are labeled as on the left of Fig. 1, with the approximate Russell-Saunders labeling on the right. The constant  $a$ ,  $b$ ,  $c$ ,  $d$  measure the departure from Russell-Saunders coupling and

<sup>6</sup> G. H. Shortley, L. H. Aller, J. G. Baker, and D. H. Menzel, *Astrophys. J.* **93**, 178 (1941); G. H. Shortley, *Phys. Rev.* **57**, 225 (1940); S. Pasternack, *Astrophys. J.* **92**, 129 (1940).

define the actual wave functions  $\psi$  for the various levels in terms of the Russell-Saunders eigenfunctions  $\varphi$ .  $s_2$  is the radial integral

$$s_2 = \int_0^\infty r^2 R^2(6p) dr.$$

The wave functions  $\psi$  are:

$$\begin{aligned}
 \psi(A_2) &= a\varphi(^1D_2) + b\varphi(^3P_2), \\
 \psi(B_2) &= -b\varphi(^1D_2) + a\varphi(^3P_2), \\
 \psi(C_0) &= c\varphi(^1S_0) + d\varphi(^3P_0), \\
 \psi(D_0) &= -d\varphi(^1S_0) + c\varphi(^3P_0).
 \end{aligned} \quad (5)$$

With  $s_2$  measured in units of the Bohr radius squared, the transition probabilities in terms of the line strengths are:

$$A_q(A, B) = \frac{3}{40} T_0 \frac{\sigma^5}{2J_A + 1} S_q(A, B),$$

magnetic dipole:

$$A_m(A, B) = T_0 \frac{\sigma^3}{2J_A + 1} S_m(A, B). \quad (6)$$

Jenkins and Mrozowski<sup>2</sup> studied the Zeeman effect of the line ( $A_2 \ ^3P_1$ ),  $\lambda 7330$ . From the formulas (3) and the line strengths we can write the transition probabilities for the various components in terms of  $s_2$ :

$M$	$M'$	Transverse to magnetic field
2	1	$G_0(3.85s_2^2 \times 10^{-5} + 0.25 - 6.2 \times 10^{-3}s_2)$
1	0	$G_0(1.93s_2^2 \times 10^{-5} + 0.125 + 3.1 \times 10^{-3}s_2)$
0	1	$G_0(5.8s_2^2 \times 10^{-5} + 0.0416 + 3.1 \times 10^{-3}s_2)$
2	0	$G_0(7.7s_2^2 \times 10^{-5})$
1	-1	$G_0(3.85s_2^2 \times 10^{-5})$
1	1	$G_0(0.25)$
0	0	$G_0(0.33)$
Parallel to magnetic field		
2	1	$G_0(7.7s_2^2 \times 10^{-5} + 0.5 + 12.4 \times 10^{-3}s_2)$
1	0	$G_0(3.85s_2^2 \times 10^{-5} + 0.25 - 6.2 \times 10^{-3}s_2)$
0	1	$G_0(11.6s_2^2 \times 10^{-5} + 0.083 - 6.2 \times 10^{-3}s_2)$
$G_0 = 3b^2\sigma^3 T_0 / 8\pi.$ (7)		

The transitions are symmetric,  $M \rightarrow M' = -M \rightarrow -M'$ .

It is seen that the intensities of the  $\Delta M = \pm 1$  transitions are quite sensitive to the value of  $s_2$ .

The experiments were only performed transverse to the magnetic field. In Tables II and III of reference 2 are summarized the observed data, the expected intensities from (7), the intensities without interference, and the theoretical intensities corrected for the influence of hyperfine structure.  $s_2$  is determined by the percentage quadrupole, defined as the ratio of electric quadrupole to magnetic dipole intensity in  $\lambda 7330$ . Jenkins and Mrozowski obtain good agreement with (7) with the assumption of 2 percent quadrupole, with an upper limit of 2.6 percent.

It is interesting to compare the value of  $s_2$  obtained from these Zeeman measurements with that deduced from Mrozowski's direct comparison of total line intensities. The coefficients  $a$ ,  $b$ ,  $c$ ,  $d$  in (5) are calculated by diagonalizing the spin-orbit matrix and then fitting to the energy levels. The necessary values of the parameters may be obtained from Robinson and Shortley.<sup>7</sup> They are  $F_2=921 \text{ cm}^{-1}$ ,  $\zeta=7290 \text{ cm}^{-1}$  and the coefficients, line strengths, and transition probabilities then have the values,<sup>8</sup> obtained from formulas (4) and (6).

$$a=0.756, \quad b=0.654, \quad c=0.927, \quad d=-0.375.$$

Quadrupole:

$$\begin{aligned} S_q(A_2 \ ^3P_1) &= 0.257s_2^2 \\ S_q(A_2 B_2) &= 1.025s_2^2 \\ S_q(A_2 D_0) &= 0.000897s_2^2 \\ S_q(B_2 D_0) &= 0.369s_2^2 \\ S_q(C_0 B_2) &= 0.229s_2^2 \\ A_q(A_2 \ ^3P_1) &= 1.133 \times 10^{-7} T_0 s_2^2 \\ A_q(A_2 B_2) &= 1.418 \times 10^{-7} T_0 s_2^2 \\ A_q(A_2 D_0) &= 3.902 \times 10^{-9} T_0 s_2^2 \\ A_q(B_2 D_0) &= 0.4754 \times 10^{-7} T_0 s_2^2 \\ A_q(C_0 B_2) &= 25.08 \times 10^{-7} T_0 s_2^2 \end{aligned} \quad (8)$$

Magnetic Dipole:

$$\begin{aligned} S_m(A_2 \ ^3P_1) &= 1.83 \\ S_m(A_2 B_2) &= 1.07 \\ S_m(C_0 \ ^3P_1) &= 0.281 \\ A_m(A_2 \ ^3P_1) &= 4.087 \times 10^{-4} T_0 \\ A_m(A_2 B_2) &= 3.484 \times 10^{-4} T_0 \\ A_m(C_0 \ ^3P_1) &= 21.47 \times 10^{-4} T_0. \end{aligned}$$

<sup>7</sup> H. A. Robinson and G. H. Shortley, Phys. Rev. **52**, 713 (1937).

<sup>8</sup> The coefficients and line strengths may also be calculated from the tables of reference 5, and lead to values for the transition probabilities differing very slightly from our own.

The observed intensity ratios are:  $I_{4618} : I_{5313} = 5.0 \pm 0.3$ ,  $I_{4659} : I_{7330} : I_{9250} = 0.023 \pm 0.006 : 1 : 0.84 \pm 0.07$ .<sup>9</sup> Comparing the observed intensities of  $\lambda 4618$  and  $\lambda 5313$  with the formulas (8) gives  $s_2^2=171$ , corresponding to 4.76 percent quadrupole, which will not fit the Zeeman data at all. It is not possible to make any further comparisons. The ratio of the intensities of  $\lambda 7330$  and  $\lambda 9250$  is practically independent of  $s_2^2$ . Thus with 4.75 percent quadrupole,  $I_{7330}/I_{9250}$  is 0.87, which is no more gratifying a fit of the observed data than 0.85, the ratio to be expected if there were no quadrupole present at all. On the other hand, the theoretical prediction of very low intensity for  $\lambda 4659$ , less than 0.002 compared to  $I_{7330}$  with  $s_2^2=171$ , is essentially accidental. It simply arises from the fact that with the parameters of Robinson and Shortley, the value of  $ad + \frac{1}{2}bc$  is 0.019. This, when squared, cuts down sharply the value of the transition probability. These parameter values differ slightly from those obtained from a least square fit to the observed energy levels, which, in turn, do not fit to better than two percent.  $a$ ,  $b$ ,  $c$ ,  $d$  cannot, therefore, be considered known to better than two percent. A two percent change in the coefficients can multiply  $ad + \frac{1}{2}bc$  by a factor of three and the transition probability by a factor of nine, which is enough to bring the theoretical intensity within the experimental error, when 5 percent quadrupole is used. The change in the coefficients is, of course, to be accompanied by the inclusion of terms from other configurations, to whose action is to be ascribed the lack of fit of the energy levels. These configuration interaction terms will contribute to the intensity through cross terms with the ground configuration, and it does not seem at all unlikely that the transition probability could be increased by another factor of three, which would bring it well within the observed value for 2 percent quadrupole.

Actually, the disparities between the Zeeman measurements and Mrozowski's values for the line intensities need not be taken too seriously. As may be seen from (7), the relative intensities

<sup>9</sup> We may add that Mrozowski also measured the ratio  $I_{5313}/I_{4659}$ , this ratio varying between 15 and 12, corresponding to having level  $A_2$  occupied a little more than 3 times as frequently as level  $C_0$ .

of the Zeeman components of  $\lambda 7330$  are independent of the coupling, so that the Zeeman measurements furnish a more unambiguous determination of the integral  $s_2$  than is possible from the comparison of line intensities. It is also probable that, despite the reduced intensities, the measurements of the Zeeman effect are capable of less experimental error than the observations on the multiplet structure. In the spectrum of a heavy element like Pb I, where the coupling is almost  $jj$ , the fine-structure lines occur in widely separated portions of the spectrum, and the computation of actual intensities from observed plate intensities requires difficult corrections for the variation of plate sensitivity. The sensitive dependence of the Zeeman intensities on  $s_2$  and the good agreement for 2 percent quadrupole would seem to indicate that, despite the complicating hyperfine structure, the Zeeman effect does give a good value for

$$s_2 = \int_0^\infty r^2 R^2(6p) dr \text{ in Pb I.}$$

This value may now be compared with estimates of the integral using hydrogenic wave functions with approximate screening constants as determined from Robinson and Shortley.<sup>7</sup> As Hartree fields have not yet been calculated for the  $6s^2 6p^2$  configuration, this is the only procedure possible. 2 percent and 4.75 percent quadrupole correspond, always using hydrogenic wave functions, to effective charges of about 20 and 15, and values of  $s_2$  of about 13 and 8. If we use the short isoelectronic sequence Pb I, Bi II to determine the slopes for the variation of  $F_2$  and  $\zeta$ , as in reference 7, we obtain, for both  $F_2$  and  $\zeta$ , effective charges of about 4, with  $s_2 \sim 180$ . The slope of the hydrogen-like formula for  $F_2$  is a slowly varying function of  $1/n^2$  as may be seen from Pasternack's equations,<sup>10</sup> and if we extrapolate to  $n=6$ , we obtain the effective charge  $Z \sim 12$ ,  $s_2 \sim 22$ . The acceptance of either experimental value for  $s_2$  forces us to conclude that using screening constants and hydrogenic wave functions gives much too large an estimate of the quadrupole moment of the transition electron in Pb I. This confirms a trend, noted by

Pasternack,<sup>10</sup> that estimates of  $s_2$  from screening constant data are always larger than more accurate evaluations with, for example, Hartree wave functions. Two percent quadrupole,  $Z \sim 20$ , corresponds, however, to a rather more tightly bound and penetrating electron than we expect, and a more accurate way of estimating  $s_2$  at this time would certainly be welcome. In addition, it might be worth while measuring the Zeeman effect parallel to the magnetic field, where the change in intensity as a result of interference is exactly opposite to that observed in transverse measurements.

#### HYPERFINE STRUCTURE OF MAGNETIC DIPOLE LINES

It is well known that the relative intensities of the components of an electric dipole line in hyperfine structure can be found from the usual theory of Russell-Saunders multiplet intensities by merely replacing the quantum numbers  $L$ ,  $S$ , and  $J$ , by  $J$ ,  $I$ , and  $F$ , and it is clear that the same correlations in the Rubiniowicz formulas will give the correct intensities for the hyperfine structure of electric quadrupole lines. It does not seem to have been pointed out, however, that the intensity ratios in the hyperfine structure of a magnetic dipole line will be the same as in an electric dipole line with the same correlations. Mrozowski noted the applicability of the intensity rules for electric dipole hyperfine multiplets to magnetic dipole multiplets in Pb I, and using these rules for the study of the mixed line  $\lambda 7330$ , was able to conclude that the percentage quadrupole was less than about 10 percent. He also remarked that the applicability of the rules needed some theoretical clarification.

The reason may be stated quite simply. The intensity ratios in electric dipole radiation are determined completely by the commutation rules between the operators  $\mathbf{J}$ ,  $\mathbf{I}$ , and  $\mathbf{F}$ , and the electric dipole moment  $\mathbf{P}$ . In particular, since  $\mathbf{P}$  commutes with  $\mathbf{I}$  and satisfies the usual commutation rule  $[\mathbf{J}, \mathbf{P}] = -i\hbar \mathbf{P} \times \mathbf{E}$ ,  $\mathbf{E} = i\mathbf{i} + j\mathbf{j} + k\mathbf{k}$ , with respect to  $\mathbf{J}$ , which are exactly the commutation laws for  $\mathbf{P}$  with  $\mathbf{S}$  and  $\mathbf{L}$ , the electric dipole hyperfine intensities are evaluated from the usual Russell-Saunders fine-structure formulas with the correlations given. Now for magnetic dipole radiation we must evaluate the matrix

<sup>10</sup> S. Pasternack, *Astrophys. J.* **92**, 129 (1940). See pp. 144 and 145.

elements of

$$\frac{e\hbar}{2mc}(\mathbf{L} + 2\mathbf{S}) + \frac{eg_N\hbar}{2Mc}\mathbf{I} = \mathbf{M} + \frac{eg_N\hbar}{2Mc}\mathbf{I}$$

for the various components of the multiplet, and with the assumption that the levels are not mixed by the nuclear interaction, that is, with the assumption that  $J$  remains a good quantum number and the Russell-Saunders formulas are applicable, all the matrix elements  $(\gamma JFM | \mathbf{I} | \gamma' J' M')$  vanish. This is because  $\mathbf{I}$  commutes with  $\mathbf{J}$  and the wave functions  $\psi$  in (5) have been chosen orthogonal for the different levels of the configuration. Therefore, all the contribution to the intensities comes from the matrix elements of  $\mathbf{M}$ , and since  $\mathbf{M}$  commutes with  $\mathbf{I}$  and satisfies the same commutation rule with respect to  $\mathbf{J}$  as does  $\mathbf{P}$ , the intensity ratios for magnetic dipole radiation in hyperfine structure will be the same as for electric dipole radiation. It is readily seen that the inclusion of terms in the wave functions due to the mixing by the nuclear interaction will, by first-order perturbation theory, give an error of order of magnitude of the ratio of hyperfine- to fine-structure splitting in the intensities as predicted from the Russell-Saunders formulas. This conclusion is valid for both electric quadrupole and

magnetic dipole radiation, as well as for light elements or for small values of  $b$  and  $d$  defined by (5). That is, the conclusion is not affected by the fact that the forbidden lines themselves only arise as a result of small departures from Russell-Saunders coupling. The effects of perturbations by terms from other configurations may also be neglected. The interaction with the nucleus cannot connect states of opposite parity and it is, therefore, not possible to introduce a term which, though present in small amount, could, by permitting electric dipole transitions, considerably affect the intensities. This explains the failure of Mrozowski to observe the line  $(C_0D_0)$ , which could become permitted for magnetic dipole transitions through coupling of the ground state with the  ${}^3P_1$  level, in some analogy with the Hg I line  $\lambda 2665.8$ . The ratio of hyperfine to fine structure splitting is almost  $10^{-5}$  which would make the intensity of  $(C_0D_0)$  at most  $10^{-8}$  the intensity of  $\lambda 4618$ .

I wish to thank Professor J. R. Oppenheimer, Dr. L. I. Schiff, and especially Dr. J. Schwinger, for their cooperation and advice during the course of this investigation. I am indebted to Professors F. A. Jenkins and S. Mrozowski for many stimulating discussions and for their kindness in letting me have their data in advance of publication.