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Theory of the Quadratic Zeeman Effect

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The experiments of Jenkins and Segrè, reported in the accompanying paper, are considered theoretically. The quadratic Zeeman effect observed in absorption to large orbits in strong magnetic fields is due to the diamagnetic term in the Hamiltonian, which is proportional to the square of the vector potential and hence to the square of the magnetic field. For the alkalis, the problem involves essentially only one electron, and its spin can be ignored. m_l and parity are always exactly defined, while n and l are not. The observed spectrum can be divided up with increasing n into three regions, according as the lines are broadened asymmetrically (region I), broadened further, but nearly symmetrically (region II), and broadened so much as to overlap into a continuum (region III). It is shown that region I corresponds to n being a good quantum number and l a fairly good one; region II to n being a fairly good quantum number and l not good at all; and region III to both n and l breaking down completely as quantum numbers. Good quantitative agreement with the experiments is obtained as long as inter-n perturbations can be neglected. When this can no longer be done (large n), the theory becomes prohibitively complicated, although some qualitative indications can still be obtained from it.

THE quadratic Zeeman effect can arise from two parts of the atomic Hamiltonian. The term linear in the vector potential (and hence in the magnetic field)

$$(e\hbar H/2mc)(m_l+2m_s) \tag{1}$$

is not a constant of the motion when there is coupling between spin and orbital angular momenta, and therefore gives rise to second-order perturbations proportional to H^2. The diamagnetic term quadratic in the vector potential

$$V=(e^2H^2/8mc^2)r^2\sin^2\theta \tag{2}$$

gives first-order perturbations that are also proportional to H^2. These two terms are never simultaneously of importance.[1] For (2) is important only for large orbits and strong magnetic fields, in which case the spin and orbital angular momenta are so completely uncoupled that (1) is practically a constant of the motion. This results in a complete Paschen-Back effect, and the electron spin can be ignored entirely. The determination of the atomic level structure under these conditions is reported by Jenkins and Segrè in the accompanying paper (referred to here as JS), and was accomplished by measuring high members of the absorption series from the ground states of sodium and potassium. In this paper, we shall attempt to obtain an understanding of the principal experimental results of JS on the basis of existing atomic theory. For definiteness, we consider sodium, and indicate later how our remarks can be extended to the other alkalis.

It was expected that the experiments of JS would show the well-known quadratic shift of the terms towards higher energies.[1] However, an examination of the microphotometer traces (Fig. 5 of JS) indicates that the situation is more complicated. The observed spectrum can be roughly divided into three regions. In region I ($n<29$), both the $\pi(m_l=0)$ and $\sigma(m_l=\pm 1)$ components show an asymmetric broadening; the peaks are on the high energy side of each line. Also, the centers of the lines lie at higher energies than the no-field lines, and the displacements increase with n. As n increases, the lines become broader, and each peak is pushed more to the high energy side of the center of gravity of its line. At the same time the peaks become lower, so that soon the lines become nearly symmetrically broadened (we call this region II, $29<n<33$). Finally the lines become so low and broad that they merge into a continuum showing a weak banded structure (region III, $n>33$). Throughout regions I and II, the centers of both the π and σ lines continue to advance ahead of the no-field lines. In region III, however, this applies only to the σ series. The π series are much more compressed and tend to fall back into step with the no-field series.

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[1] Cf. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford, 1932), p. 178.

To understand these results, we consider the motion of a single electron in a central field (nucleus plus electron core) and uniform external magnetic field, with neglect of spin. The problem possesses only axial and mirror symmetry, and hence m_l and parity only are exactly defined; the term (2) in the Hamiltonian will prevent n and l from being exact quantum numbers for the terms that interest us. Then the true eigenfunctions can give dipole radiation only by virtue of the amount of $l=1$ state that is mixed into them; moreover, we can restrict our consideration to those upper states for which $m_l=0, \pm 1$. If we choose the usual representation for the unperturbed states in which m_l, n and l are diagonal, then it is readily shown that V has matrix elements between states of all n provided that their l values differ by $0, \pm 2$; since only the $l=1$ part of the perturbed states can radiate, we need consider only the matrix elements of V between states of odd l.

Now according to the Rydberg formula, the P terms in sodium ($l=1$) are depressed by a uniform amount below the corresponding hydrogenic terms (this is due to penetration of the core by the electron when it has low angular momentum), while the $F, H, \cdots$ terms ($l=3, 5, \cdots$) are given quite accurately by the hydrogenic values (see Fig. 6 of JS). The matrix elements of V are proportional to n^4 (see Eq. (3) below), while the separations between successive terms in a series or between corresponding P and F terms are proportional to n^{-3}. Thus, we expect that for small n these separations are large compared to the perturbing energy, and both n and l should be fairly good quantum numbers (region I). Moreover, since the separation between corresponding P and F terms is smaller than the separation between successive terms of a series, we might expect n to be a better quantum number than l, so that we can neglect the inter-n perturbations, and treat the inter-l perturbations as small, in this region. Now the quantum defect for the P series of sodium is 0.85, so that each P term is depressed almost a whole interval below the F, $H, \cdots$ terms of the same n. Thus the important inter-l perturbations will be between a given P term and the $F, H, \cdots$ terms corresponding to an n value that is smaller by one; the P term then lies on the high energy side of the higher l terms with which it combines. This results in a peak on the high energy side of the line, and a smear on the low energy side which is the group of unresolved lines arising from the slightly mixed in terms of higher l. As n increases, l ceases to be a good quantum number before n does. Thus all l terms are thoroughly mixed together, resulting in a nearly symmetric line, while the inter-n perturbations are not yet so large as to seriously affect the regularity of the series (region II). For still higher n values (region III), the inter-n perturbations become so large that n is no longer a good quantum number, and the broadened lines merge together.

REGIONS I AND II

We could hope to deal with regions I and II by neglecting inter-n perturbations, and solving the secular equation obtained from the matrix elements of V between odd l states for a particular m_l and n. But since this matrix has about $n/2$ rows and columns, such a solution would be an extremely tedious matter. However, we can find quite simply the centers of gravity of the broadened lines and their mean square breadths. In region I, we can also find the perturbation of each P state by higher l states consistently to the second order of perturbation theory, and can interpret its perturbed position as the position of the peak of the corresponding broadened line.

To find the matrix of V in these regions, we choose particular values for m_l and n, and label rows and columns according to l values. The angle integrals are readily evaluated, and the only nonvanishing elements that interest us are V_{11}, $V_{13}=V_{31}$, V_{33}, $V_{35}=V_{53}$, etc. In evaluating the radial integrals, we note that because of the r^2 appearing in V, it is important to know the radial functions only for large r, well outside of the inner electronic core. We should thus expect to obtain a good approximation for the radial integrals by using the hydrogenic functions[2] with indices n and l, and putting $n=n^*$ (the effective quantum number) after the integrals are evaluated. For the principal series of sodium ($l=1$), $n^*=n-0.85$, while for the higher series ($l=3, 5, \cdots$), $n^*=n$. As remarked above, however, we expect the mutual perturbations between states

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[2] Cf. Condon and Shortley, *Theory of Atomic Spectra* (Cambridge, 1935), p. 114.

of different l to be greatest when their effective quantum numbers (and hence their unperturbed energies) lie closest together. We shall therefore put for the higher l series, $n^* = n-1$. The total energy matrix for a particular m_l and n is:

$$\begin{aligned}
\mathcal{H}_{ll'}(n, m_l) &= \mathcal{H}_l^0(n, m_l)\delta_{ll'} + V_{ll'}(n^*, m_l),\\
\mathcal{H}_l^0(n, m_l) &= -\frac{me^4}{2\hbar^2 n^{*2}} + \frac{e\hbar H m_l}{2mc},\\
V_{ll}(n, 0) &= \frac{\hbar^4 H^2}{8m^3c^2e^2} \cdot \frac{n^2[5n^2+1-3l(l+1)](l^2+l-1)}{(2l+3)(2l-1)},\\
V_{l,\,l-2}(n, 0) &= -\frac{\hbar^4 H^2}{8m^3c^2e^2} \cdot \frac{5n^2 l(l-1)}{2(2l-1)} \cdot \left\{\frac{(n^2-l^2)[n^2-(l-1)^2]}{(2l+1)(2l-3)}\right\}^{\frac{1}{2}},\\
V_{ll}(n, \pm 1) &= \frac{\hbar^4 H^2}{8m^3c^2e^2} \cdot \frac{n^2[5n^2+1-3l(l+1)]l(l+1)}{(2l+3)(2l-1)},\\
V_{l,\,l-2}(n, \pm 1) &= -\frac{\hbar^4 H^2}{8m^3c^2e^2} \cdot \frac{5n^2}{2(2l-1)} \cdot \left\{\frac{(n^2-l^2)[n^2-(l-1)^2](l+1)l(l-1)(l-2)}{(2l+1)(2l-3)}\right\}^{\frac{1}{2}}.
\end{aligned} \tag{3}$$

To obtain some information from the matrix (3), we assume that it is diagonalized by a normalized real orthogonal matrix S (since $\mathcal{H}$ is real): $\sum_{kl} S_{ik}\mathcal{H}_{kl}S_{jl} = E_i\delta_{il}$. Then the new eigenfunctions (corresponding to the eigenvalues E_i) are given in terms of the old approximately hydrogenic functions by: $\phi_i = \sum_j S_{ij}\psi_j$. If now we neglect the dependence of the dipole radiation probability on energy over the small range of energies involved in this group of states, this probability will be proportional to the square of the amount of ψ_1 in each ϕ_i, or to S_{i1}^2. The center of gravity of the group of lines is thus given by

$$\bar{E} = \sum_i E_i S_{i1}^2 = \mathcal{H}_{11}. \tag{4}$$

The dispersion of the group of lines about their center of gravity, or the mean square breadth of the unresolved broadened line, will similarly be given by:

$$\begin{aligned}
(\Delta E)^2 &= \sum_i (E_i - \bar{E})^2 S_{i1}^2 = \sum_i E_i^2 S_{i1}^2 - \bar{E}^2\\
&= \sum_j \mathcal{H}_{1j}^2 - \bar{E}^2 = \mathcal{H}_{13}^2,
\end{aligned} \tag{5}$$

since $\mathcal{H}_{1j}$ vanishes unless $j=1$ or 3. Neglecting terms of order n^{-2} compared to unity, we thus obtain:

$$\begin{aligned}
\bar{E}(n, 0) &= -\frac{me^4}{2\hbar^2 n^{*2}} + \frac{\hbar^4 H^2 n^{*4}}{8m^3c^2e^2},\\
\bar{E}(n, \pm 1) &= -\frac{me^4}{2\hbar^2 n^{*2}} \pm \frac{e\hbar H}{2mc} + \frac{\hbar^4 H^2 n^{*4}}{4m^3c^2e^2};
\end{aligned} \tag{6}$$

$$\begin{aligned}
2\Delta E(n, 0) &= \left(\frac{3}{7}\right)^{\frac{1}{2}} \cdot \frac{\hbar^4 H^2 n^{*4}}{4m^3c^2e^2},\\
2\Delta E(n, \pm 1) &= \left(\frac{2}{7}\right)^{\frac{1}{2}} \cdot \frac{\hbar^4 H^2 n^{*4}}{4m^3c^2e^2}.
\end{aligned} \tag{7}$$

In Eq. (6), $n^* = n - 0.85$; in Eq. (7) we should use a value for n^* approximately halfway between $n-0.85$ and $n-1$, although its precise value is not important. Eq. (6) is well known,[1] and gives the position of the P term if inter-l perturbations are neglected. It is interesting that the center of gravity of the group of lines resulting from these perturbations is still given by the same formula.

Although formulas (6) and (7) apply to both regions I and II, we are, for region I, more interested in the position of the peak E_p of each line than in $\bar{E}$. This can be found by assuming that the inter-l perturbations are not yet strong enough to wipe out the identity of the P state, so that this line will be strongest, and will be shifted towards higher energy by interaction with the other l states. A second-order perturbation calculation gives:

$$E_p = \mathcal{H}_1^0 + V_{11} + \sum_{i \neq 1} \frac{V_{1i}^2}{\mathcal{H}_1^0 - \mathcal{H}_i^0}. \tag{8}$$

Remembering that V_{1i} vanishes unless $i=1$ or 3, and that

$$\mathcal{H}_1^0 - \mathcal{H}_3^0 = -\frac{me^4}{2\hbar^2}[(n-0.85)^{-2} - (n-1)^{-2}] \approx \frac{me^4\Delta}{\hbar^2 n^{*3}},$$

where $\Delta = 0.15$, we obtain:

$$E_p(n,\,0) \approx \bar{E}(n,\,0) + \frac{3\hbar^{10}H^4 n^{*11}}{448 m^7 c^4 e^8 \Delta},$$
$$E_p(n,\,\pm 1) \approx \bar{E}(n,\,\pm 1) + \frac{\hbar^{10}H^4 n^{*11}}{224 m^7 c^4 e^8 \Delta}, \tag{9}$$

where to sufficient approximation, $n^* = n - 0.85$. We expect formula (9) to give the position of the peak of the broadened line as long as the peak is well defined and displaced from the center of gravity of the line, that is, throughout region I. In region II, the line is more nearly symmetric, and the peak and center of gravity practically coincide, their position being given by (6).

The transition from region I to region II should take place at such a value n_c of n that the perturbing energy V_{13} and the energy denominator $\mathcal{H}_1{}^0 - \mathcal{H}_3{}^0$ in (8) are about equal. This gives us the relations:

$$(n_c - 0.85)^7 \approx \left(\frac{7}{3}\right)^{\frac{1}{2}} \cdot \frac{8m^4c^2e^6\Delta}{\hbar^6 H^2}, \quad m_l = 0,$$
$$\approx \left(\frac{7}{2}\right)^{\frac{1}{2}} \cdot \frac{8m^4c^2e^6\Delta}{\hbar^6 H^2}, \quad m_l = \pm 1. \tag{10}$$

To obtain similar results for the other alkalis, we need only insert into the above formulas (6) to (10) the proper numerical values for n^* and for Δ, which is defined as the effective quantum number for the P series minus the nearest integer; these values are given in Table III of JS.

The measured peaks of the lines are plotted in Figs. 3 and 4 of JS, in which the solid curves are computed from Eq. (6) and the dotted curves are computed from Eq. (9). It will be noted that the experimentally observed peaks follow the dotted curves quite well throughout region I. Towards the end of region I and the beginning of region II, the lines lose their asymmetric character, and the measured peaks begin to give the positions of the centers of gravity of the lines. Thus the experimental points here fall away from the dotted curves and approach the solid curves. This good agreement indicates that the inter-n perturbations in this region do not have an appreciable effect on the positions of the peaks of the lines. On the other hand, the breadths of the lines seem to be given well by Eq. (7), only for rather small values of $n (<25)$. For larger n, the values obtained from Eq. (7) are of the same order of magnitude, but smaller than, the observed values. This seems to indicate that the inter-n perturbations, which were neglected in obtaining (7), do broaden out the lines, and also make the ratio of π to σ breadth larger than the value $(3/2)^{\frac{1}{2}} = 1.22$ obtained from (7) (see Table II of JS). The comparison with experiment on this point is complicated by the fact that the mean square breadth defined by (5), and which is most readily calculated, is not simply related to the width at half-maximum, which is most readily measured; however, the two should be of the same order of magnitude.

The value of n at which the transition from region I to region II takes place is given by Eq. (10) as about 29 for the π component, and about 30 for the σ components, in the case of sodium. From Fig. 5a of JS, we see that both these values agree well with experiment. A comparison on this point for potassium is difficult because of the poor definition of the lines.

REGION III

In region III, both n and l break down completely as quantum numbers, and we cannot use any of the approximations that made the theory workable in the preceding section. There is a striking experimental observation in this region, however, for which we might hope to get an indication from the theory. This is the compression of the π series relative to the σ series, just before they wash out. One might expect this from the fact that in region II, the π components are much broader than the σ components, thus indicating a greater influence of inter-n perturbations. Then since there are more terms above a given term than below it, and since they get closer together as one goes up the series, the net effect of such perturbations should be to push the terms down and thus compress the series.

Another indication pointing towards the same conclusion can be obtained from an examination of the behavior of the terms near the series limit. Here the electron is controlled mainly by the magnetic field, and it makes many oscillations in this field before it makes one in the Coulomb field. This is the condition for applicability of the adiabatic approximation, which we use here. The solutions of the equations of motion of an electron in a pure magnetic field are well known,[3] and admit of a continuum of energy levels

$$E=(e\hbar H/2mc)(2\nu+m_l+|m_l|+1)+E_z,\quad \nu=0,1,2,\cdots,E_z\geqq 0, \tag{11}$$

because of the free motion along the field (z direction). We now apply the adiabatic approximation, using the Coulomb field to restrict the motion in the z direction. This gives us a potential for the z motion that is an average of the Coulomb field over the x, y plane for each value of z. We are interested only in the lowest state $\nu=0$, and in $m_l=0$, ± 1; the z potential is then:

$$\begin{aligned} U_0(z)&=-2e^2\beta^{\frac{1}{2}}\exp(\beta z^2)Erfc(|z|\beta^{\frac{1}{2}}),\quad m_l=0,\\ U_1(z)&=-e^2[\beta|z|+\beta^{\frac{1}{2}}\exp(\beta z^2)(1-2\beta z^2)\\ &\quad\times Erfc(|z|\beta^{\frac{1}{2}})],\quad m_l=\pm 1,\\ U_0(0)&=2U_1(0)=-e^2(\pi\beta)^{\frac{1}{2}},\\ &U_0\rightarrow U_1\rightarrow -e^2/|z|,\quad \text{as}\quad |z|\rightarrow\infty;\\ &Erfc(x)\equiv\int_x^\infty e^{-t^2}dt;\\ &\beta\equiv eH/2\hbar c. \end{aligned} \tag{12}$$

Thus U_0 had twice the depth of U_1 at $z=0$ and the same asymptotic form; it can also be shown quite readily that U_0 is less than U_1 for all finite values of z. The total energy is then given approximately by (11), where E_z is now an eigenvalue of the equation:

$$\frac{d^2\chi}{dz^2}+\frac{2m}{\hbar^2}[E_z-U(z)]\chi=0.$$

Then for energies just below the series limit, the eigenvalues for the case $m_l=0$ will be more closely spaced than those for the case $m_l=\pm 1$, since the potential U_0 is considerably deeper than the potential U_1. While this conclusion cannot apply even qualitatively as far from the series limit as the beginning of region III, it serves as another indication that the π component series is expected to be more compressed than the σ component series, as is observed.

It is a pleasure for us to thank Professor J. R. Oppenheimer for several helpful discussions of points that arose in this problem.

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[3] Cf. Condon and Morse, *Quantum Mechanics* (McGraw-Hill, 1929), p. 79.

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Surface and Volume Photoelectric Emission from Barium[1]

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Spectral sensitivity measurements between 5000 and 2300A have been made on barium surfaces prepared by fractional distillation in a gettered vacuum. The resulting yields are compared with those predicted by Mitchell's square-top barrier theory which is here modified to a form that facilitates comparison with experimental data. From 5000 to 3000A relative values of the observed yields are in good agreement with the modified theory. At 2967A there is an abrupt rise in the experimental curve which continues to the limit of the measurements. This is attributed to the onset of the volume photoelectric effect. The theoretical threshold for the volume effect calculated from the rough formulae of Tamm and Schubin agrees well with the experimental value.

IT is usually assumed in the electron theory of metals that the electrons move independently in a periodic potential field in the metal. The introduction of a metallic surface which is necessary for the photoelectric effect gives rise to a second type of field and complicates the model by destroying the perfect periodicity of the crystal lattice. To avoid this difficulty Tamm and

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[1] Presented in part at the Washington meeting of the American Physical Society, April 28–30, 1938.

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