

components. These measurements enable the sketching in of the microphotometer traces with intensity as ordinates and position of the components as abscissae. These traces are placed one above the other to show the progressive change in the pattern as magnetic fields of greater and greater strength were applied. The results for the perpendicular components are shown in Fig. 5 and the parallel components in Fig. 6. In both of these figures the vertical lines or the lines at a small angle from the vertical represent the theoretical splitting for the even-numbered isotopes as shown in Fig. 1 and for the odd-numbered isotopes as shown in Figs. 3 and 4. The splittings for the even-numbered and the odd-numbered isotopes are shown as full and dotted lines, respectively. The perpendicular components show $\frac{3}{2}$ splitting which is to be expected on the basis of Schuler and Keyston's

explanation and which has previously been reported by MacNair.⁵ The examination of the experimental results for the parallel components show that the -10.3 component shifts toward the zero component in agreement with the theoretical prediction of Darwin's theory but which for the range of fields used is not in agreement with the results of MacNair.

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The Paschen-Back Effect

V. Theory of the Effect for Intermediate Coupling

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General spectroscopic theory has been applied to the Paschen-Back effect and simplified methods developed for determining the positions of the energy levels and intensities of lines for cases of intermediate coupling. They are expressed in terms of *LS*-coupling as the zero-order functions.

A COMPLETE theory of the Paschen-Back effect for intermediate coupling in two-electron spectra was first given by Houston¹ (in essence) for the case of one electron in an *s* state and was later completed and experimentally verified by Green and Loring² and by Jacquinet.³ Houston's zero-order approximation, while satisfactory for the particular example studied, proves unwieldy, however, when applied to more complicated configurations. Since the

publication of Houston's paper, a very considerable body of theoretical work has been carried out, and spectroscopic theory has been advanced to the point where the problem of the Paschen-Back effect can be stated in general terms for any kind of coupling. While it is useful to be able to state the general solution to any problem, it is the actual application of the problem to particular cases that is of prime interest to the experimental physicist; and it is the purpose of the present paper to express the solution in terms that are very easily interpreted in terms of a coupling system that is familiar to everybody; namely, *LS*-coupling.

¹ W. V. Houston, *Phys. Rev.* **33**, 297 (1929).

² J. B. Green and R. A. Loring, *Phys. Rev.* **46**, 888 (1934).

³ P. Jacquinet, Thesis, (Paris, 1937).

I. CALCULATION OF ENERGY LEVELS

Let us suppose that using the *LS*-coupling scheme we can write part of the matrix of a given configuration involving the two *j* values *j* and *j*+1, in the following manner.

$$\begin{array}{c}
 \begin{array}{c}
 s_{Lj} \quad s^{-1}L_j \quad s_{(L-1)j} \quad s_{Lj+1} \quad s_{(L+1)j+1} \quad s_{(L-1)j+1} \\
 \begin{array}{c}
 s_{Lj} \\
 s^{-1}L_j \\
 s^{-1}(L-1)j \\
 s_{Lj+1} \\
 s_{(L+1)j+1} \\
 s_{(L-1)j+1}
 \end{array}
 \end{array}
 \begin{array}{|c|c|c|}
 \hline
 A & a & b \\
 \hline
 B & B & c \\
 \hline
 C & c & C \\
 \hline
 D & d & e \\
 \hline
 E & d & E & f \\
 \hline
 F & e & f & F \\
 \hline
 \end{array}
 \end{array}
 \quad (1a)$$

where the lower case letters represent magnetic interaction terms arising from spin-orbit interaction, and the upper case letters represent, in general, electrostatic plus magnetic (spin-orbit) interaction energies. In a large number of cases, especially for two-electron spectra, these terms have been calculated⁴ in terms of certain parameters representing radial integrals. It is possible, then, from the known energy levels of a given spectrum, to work backwards and determine the values of the parameters. Let us suppose that the observed energy levels are *A'*, *B'*, *C'*, *D'*, *E'*, *F'*. This is equivalent to saying that we have determined a transformation.

$$g_i = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)},$$

$$k \text{ and } l = \left[\frac{(J-L+S+1)(J+L-S+1)(J+L+S+2)(L+S-J)}{4(J+1)^2(2J+1)(2J+3)} \right]^{\frac{1}{2}} [(J+1)^2 - m^2]^{\frac{1}{2}}$$

and are diagonal, while nondiagonal terms occur only between terms with *J*'s differing by unity but with the same *S* and *L*.

If we apply the transformation (2) to this matrix, and add the result to the diagonalized matrix in the absence of the magnetic field, the problem of the determination of the energy levels is complete.

To make the case simple, suppose that three of the levels, *A'*, *B'*, *D'* are sufficiently close so that they will perturb each other in the presence

⁴ See e.g., E. U. Condon, and G. H. Shortley, *Atomic Spectra* (Cambridge University Press, 1934).

$$\begin{array}{c}
 \begin{array}{c}
 s_{Lj} \quad s^{-1}L_j \quad s_{(L-1)j} \quad s_{Lj+1} \quad s_{(L+1)j+1} \quad s_{(L-1)j+1} \\
 A_j' \\
 B_j' \\
 C_j' \\
 D_{j+1}' \\
 E_{j+1}' \\
 F_{j+1}'
 \end{array}
 \begin{array}{|c|c|c|}
 \hline
 a_1 & b_1 & c_1 \\
 \hline
 a_2 & b_2 & c_2 \\
 \hline
 a_3 & b_3 & c_3 \\
 \hline
 d_1 & e_1 & f_1 \\
 \hline
 d_2 & e_2 & f_2 \\
 \hline
 d_3 & e_3 & f_3 \\
 \hline
 \end{array}
 \end{array}
 \quad (2a)$$

which transforms the matrix (1) into a diagonal matrix. These transformation coefficients are normalized and orthogonal, i.e., if $a_1^2 + a_2^2 + a_3^2 = 1$, etc. and $a_1a_2 + b_1b_2 + c_1c_2 = 0$, etc.

In the presence of a magnetic field, there is, in addition to the matrix of the energies represented by (1), a matrix resulting from the interaction of *L* and *S* with the magnetic field, which may be represented for each value of the magnetic quantum number *m*, in the following manner

$$\begin{array}{c}
 \begin{array}{c}
 s_{Lj} \quad s^{-1}L_j \quad s_{(L-1)j} \quad s_{Lj+1} \quad s_{(L+1)j+1} \quad s_{(L-1)j+1} \\
 s_{Lj} \\
 s^{-1}L_j \\
 s_{(L-1)j} \\
 s_{Lj+1} \\
 s_{(L+1)j+1} \\
 s_{(L-1)j+1}
 \end{array}
 \begin{array}{|c|c|c|}
 \hline
 mg_1\omega & 0 & 0 \\
 \hline
 0 & mg_2\omega & 0 \\
 \hline
 0 & 0 & mg_3\omega \\
 \hline
 k\omega & 0 & 0 \\
 \hline
 0 & 0 & 0 \\
 \hline
 0 & 0 & l\omega \\
 \hline
 k\omega & 0 & 0 \\
 \hline
 0 & mg_4\omega & 0 \\
 \hline
 0 & 0 & mg_5\omega \\
 \hline
 0 & 0 & mg_6\omega \\
 \hline
 \end{array}
 \end{array}
 \quad (3a)$$

where $\omega = ehH/4\pi\mu_0c$, and the *g*'s are the Landé *g*-factors

of a magnetic field. The part of the final matrix which then becomes important for the calculations of *A''*, *B''*, *D''* (the altered positions of *A'*, *B'*, *D'* in a strong magnetic field) is

$$\begin{array}{c}
 \begin{array}{c}
 A'_{i,m} \quad B'_{i,m} \quad D'_{j+1,m} \\
 A'_{i,m} \\
 B'_{i,m} \\
 D'_{j+1,m}
 \end{array}
 \begin{array}{|c|c|c|}
 \hline
 A' + mg_1'\omega & mv\omega & w\omega \\
 \hline
 mv\omega & B' + mg_2'\omega & y\omega \\
 \hline
 w\omega & y\omega & D' + mg_3'\omega \\
 \hline
 \end{array}
 \end{array}
 \quad (4a)$$

(*C'*, *E'*, *F'* are so distant that their effects on *A''*, *B''*, *D''* are negligible), where $g_i' = a_i^2 g_1$

$+b_i^2g_2+c_i^2g_3$, which represents the weak-field magnetic splitting factor in the intermediate coupling,

$$\begin{aligned} v &= a_1a_2g_1+b_1b_2g_2+c_1c_2g_3 \\ w &= a_1d_1k+c_1f_1l \\ y &= a_2d_1k+c_2f_1l. \end{aligned}$$

If we now subtract E from each of the diagonal terms of (4) and set the determinant of this matrix equal to zero, the three roots will represent the positions of the energy levels when a magnetic field is present. One noteworthy fact now becomes evident from (4). In LS -coupling there is no nondiagonal element between two terms with the same value of J . In intermediate coupling, these terms may be as large as any of the other terms introduced by the magnetic field.

II. THE INTENSITIES

The calculation of the intensities of the components involved in a transition between the configuration discussed above and another configuration whose transformation matrix is given below (5), is a much more tedious process

$$\begin{array}{cccc} & {}^sL_{j+1} & {}^s(L+1)_{j+1} & {}^{s-1}(L-1)_{j+1} & {}^s(L-1)_{j+1} \\ \begin{array}{l} H_{j+1}' \\ K_{j+1}' \\ L_{j+1}' \\ N_{j+1}' \end{array} & \begin{array}{|c|c|c|c|} \hline h_1 & k_1 & l_1 & n_1 \\ \hline h_2 & k_2 & l_2 & n_2 \\ \hline h_3 & k_3 & l_3 & n_3 \\ \hline h_4 & k_4 & l_4 & n_4 \\ \hline \end{array} & & & \end{array} \quad (5a)$$

(In the following example the above configuration is spread out sufficiently so that no Paschen-Back effect in this configuration need be considered.)

If we neglect the quantities depending on the numbers of atoms in the different states and the factors depending on the frequency, then the matrix of the square roots of the line strengths in a particular transition may be written as in

$$\begin{array}{cccc} & {}^sL_{j+1, m+1} & {}^s(L+1)_{j+1, m+1} & {}^{s-1}(L-1)_{j+1, m+1} & {}^s(L-1)_{j+1, m+1} \\ \begin{array}{l} {}^sL_{j, m} \\ {}^{s-1}L_{j, m} \\ {}^s(L-1)_{j, m} \\ {}^sL_{j+1, m} \\ {}^s(L+1)_{j+1, m} \\ {}^s(L-1)_{j+1, m} \end{array} & \begin{array}{|c|c|c|c|} \hline p & q & 0 & t \\ \hline 0 & 0 & r & 0 \\ \hline s & 0 & 0 & u \\ \hline \alpha & \beta & 0 & \gamma \\ \hline \delta & \epsilon & 0 & 0 \\ \hline \zeta & 0 & 0 & \xi \\ \hline \end{array} & & & \end{array} \quad (6a)$$

(6). (This procedure is justifiable, since we are usually dealing with an extremely small frequency interval in the Paschen-Back effect.) (6) represents the (strengths)^½ of transitions between levels j, m and $j+1, m$ of one configuration, and $j+1, m+1$ of another configuration.

Operating on (6) on the left by (2) and on the right by (5) transposed we obtain the matrix of $S^{\frac{1}{2}}$ in the type of coupling involved, in the absence of the magnetic field. The individual matrix elements are of the following form:

$$\begin{aligned} (A'jm|S^{\frac{1}{2}}|H'j+1m+1) &= (a_1p+c_1s)h_1 \\ &\quad + a_1qk_1+b_1rl_1+(a_1t+c_1u)n_1 \\ (E'j+1m|S^{\frac{1}{2}}|L'j+1m+1) &= (d_2\alpha+e_2\delta+f_2\zeta)h_3+(d_2\beta+e_2\epsilon)k_3 \\ &\quad + 0 \cdot l_3+(d_2\gamma+f_2\xi)n_3. \end{aligned} \quad (7a)$$

The squares of these quantities would represent the line-strengths in a weak magnetic field.

If, now, a strong magnetic field is introduced it is necessary to diagonalize (4) before we can calculate the matrix of $S^{\frac{1}{2}}$. With the same approximations as in (4) the transformation matrix is

$$\begin{array}{ccc} & A'_{j, m} & B'_{j, m} & D'_{j+1, m} \\ \begin{array}{l} A''_m \\ B''_m \\ D''_m \end{array} & \begin{array}{|c|c|c|} \hline a_1' & a_2' & a_3' \\ \hline b_1' & b_2' & b_3' \\ \hline d_1' & d_2' & d_3' \\ \hline \end{array} & & \end{array} \quad (8a)$$

(To be exact, we should include terms a_4', a_5', a_6' , etc. due to interactions between A', B', D' , and C', E', F' , but these are negligible in the case considered.) Then the line-strength of the component for $A''_{j, m} \rightarrow H''_{j+1, m+1}$ (the values of A' and H' in a strong magnetic field) is given (approximately) by

$$\begin{aligned} & [(A''jm|S^{\frac{1}{2}}|H''j+1m+1)]^2 \\ &= [a_1' \{ (a_1p+c_1s)h_1+a_1qk_1+b_1rl_1 \\ &\quad + (a_1t+c_1u)n_1 \} + a_2' \{ (a_2p+c_2s)h_1 \\ &\quad + a_2qk_1+b_2rl_1+(a_2t+c_2u)n_1 \} \\ &\quad + a_3' \{ (d_1\alpha+e_1\delta+f_1\zeta)h_1 \\ &\quad + (d_1\beta+e_1\epsilon)k_1+0 \cdot l_1+(d_1\gamma+f_1\xi)n_1 \}]^2 \end{aligned} \quad (9a)$$

and similarly for the other components.

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