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AN EXTENSION OF HOUSTON'S AND SLATER'S MULTIPLET RELATIONS

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Abstract

Expressions giving the change in the positions of the energy levels with change in electron coupling are derived. The change in g-values is discussed also. The method of derivation is a short-cut of the rigorous detailed method and therefore simpler. One knows the form of the equations of which the desired energies must be roots. The coefficients of these equations are determined by the known results for extreme couplings. This method does not always give all coefficients, but even in complicated cases useful relations between the energy levels are found.

For the case of two electrons one of which is in an s-state, Houston[1] obtained expressions for the four resulting levels for any coupling strength. Houston considered the coupling and the spin-orbit interaction as perturbations and calculates by quantum mechanics the first order perturbations to the energy. He also derived expressions for the g-values and for the intensities to show their variation with change of coupling.

As soon as one removes the restriction that one of the two electrons is in an s-state the method used by Houston becomes very complicated. Dr. Laporte has informed me that one can apply Houston's results to configurations like p^5s and d^9s by considering the p^5 and the d^9 group as if it were a single p, or d electron and by taking, in addition, the spin orbit interaction with a negative sign. This remark led to the considerations outlined in this paper.

It is possible to get the main results and often even the complete results of the detailed theory as used by Houston by a simplified procedure. One knows from perturbation theory exactly what type of equations will be obtained for the first order perturbations to the energy. Furthermore one knows from simple considerations of the vector model the energies in extreme (j, j) coupling and in the extreme Russell-Saunders coupling.[2] In the latter case the results of the vector model have to be supplemented with the results derived by Slater[3] which give relations among the distances of various multiplets of a configuration. Our knowledge of these extreme cases is sufficient to fix the most important coefficients, sometimes all coefficients, in the general equation for the energy perturbation.

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

[2] Extreme (j,j) coupling means no interaction between the electrons, extreme Russell-Saunders coupling large interaction, much larger than the interaction between spin and orbit.

[3] J. C. Slater, Phys. Rev. **34**, 1293, (1929).

From the formulas obtained in this way one hopes to be able to predict the position of unknown levels but in this respect the results are rather disappointing. First of all one must not forget that we consider only the first order perturbation; thus neither the coupling nor the spin-orbit interaction may be too large. This excludes the very light and the very heavy elements. In the former the singlet-triplet and similar distances are often of the same order as the total energy, in the latter this is the case for multiplet separations. But much worse for their use as predictors of levels is the special form which most of the resulting expressions have. Consider for instance a triplet and a connected singlet level. If one knows the singlet and two levels of the triplet one can predict with great accuracy the position of the third triplet level. This great accuracy, however, is due to the fact that this triplet level is not displaced very much in going from one extreme coupling to the other. A mere guess would have given a fair result. In practice, on the contrary, one always knows the triplet and wants to know the position of the singlet. Its variation in position with change of coupling is very large and a small error in the known triplet causes a large error in the predicted position of the singlet. Of course the percentage error one makes in predicting the triplet level is the same as for the singlet level, but for the latter this corresponds to a much larger absolute error in position. In general the predictions will be most accurate if the singlet is not very far away from the triplet. It is to be regretted that in practice one just always needs the cases where the prediction is most unusable! What is said here for the simple example of a singlet and a triplet holds also for more complicated cases.

Before demonstrating the method by examples we will describe the general equation for the energy perturbation mentioned above. Let us denote the perturbation energies by X_1, X_2, ... For instance in the case of two electrons X_1 is the coupling energy, X_2 and X_3 are the spin orbit interactions[4] for both electrons, X_4 might be the energy in an external magnetic field in case we want the g-values, etc. If, in the configuration which we consider, a certain value of the total moment J occurs for n levels, their energy perturbations E will be the roots of an equation of the nth degree, homogeneous in E and all the X's.

$$E^n + E^{n-1}\Sigma a_k X_k + E^{n-2}\Sigma b_{kl} X_k X_l + E^{n-3}\Sigma c_{klm} X_k X_l X_m + \cdots = 0. \quad (1)$$

It is obvious that only in a few cases our knowledge of the extreme couplings is sufficient to determine *all* the unknown coefficients. But we can be glad that such rather simple cases form quite an interesting group for which there is a large amount of known material and which is also of some interest with regard to the prediction of levels.

In more complicated cases not all coefficients can be found. For example, the coefficients of products of different X's are often not obtainable by our method. But even if we know only the first coefficient, that of E^{n-1}, it gives

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[4] We neglect the interaction between the one spin and the other orbit. See W. Heisenberg. Zeits. f. Physik **39**, 499 (1926).

us interesting information. This coefficient is the sum of the roots, with the negative sign, and is, as we see from (1), a linear function of the perturbation energies. From this one can derive relations among the energies similar to the constancy of g-, Γ-, and intensity sum rules.

DEMONSTRATION OF THE METHOD BY EXAMPLES

The configuration p^4. As we are dealing with equivalent electrons we have only one coupling parameter X and one parameter to measure the spin orbit interaction, which will be denoted by A. This configuration gives rise to one level with $J=1$, two with $J=2$ and also two with $J=0$. In the extreme Russell-Saunders coupling they would be arranged in an inverted ${}^3P$, a ${}^1D$ and a ${}^1S$. The total separation of the triplet is equal to the doublet separation which one of the p electrons would show if it alone were present.[5] We will measure the energies in wave number units and for convenience put the ideal triplet separation equal to $3A$. The arrangement in the extreme (j, j) coupling can be found as follows.[6] The lowest state will have as many electrons as are allowed by the Pauli principle with their individual $j=\frac{1}{2}$. Thus in this state there are two electrons with $j=\frac{1}{2}$ and the remaining two have $j=1\frac{1}{2}$,

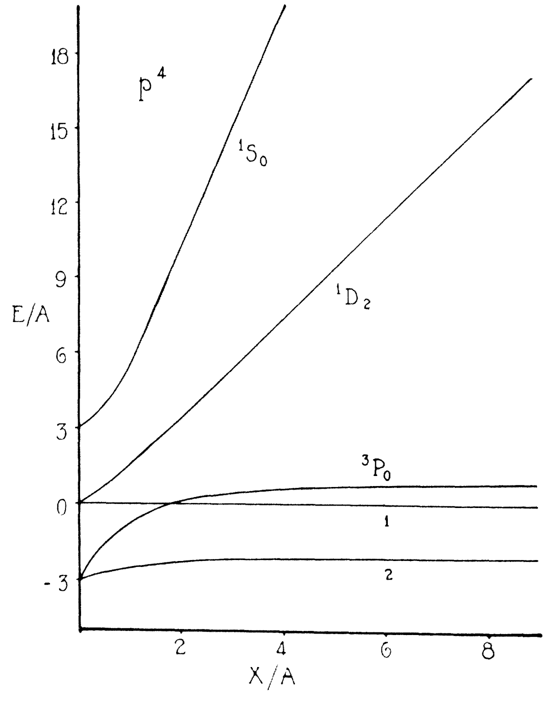

Fig. 1. Change in coupling for configuration p^4.

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[5] S. Goudsmit, Phys. Rev. **31**, 946 (1928).

[6] L. Pauling and S. Goudsmit, The Structure of Line Spectra, McGraw-Hill 1930, page 256.

giving rise to one level with $J=2$ and another with $J=0$. Next higher will be the state with one electron with $j=\frac{1}{2}$ and three with $j=1\frac{1}{2}$, producing two levels with $J=0$ and 1. The distance between these levels and the former group will be just the doublet separation of one of the p electrons, as just one changed its j from $\frac{1}{2}$ to 1 and this is again the distance which we call $3A$. Finally again $3A$ higher lies one level with $J=0$ which results from all four electrons having $j=1\frac{1}{2}$. In Figure 1 the left side represents the extreme (j,j) coupling, the right side tends to the extreme Russell-Saunders coupling. As reference level we will take the single level with $J=1$ and give the other levels by their distance E from this level.[7] Our equations (1) are thus for this example:

$$\begin{aligned} J &= 1: E_1 = 0 \\ J &= 0: E_0^2 + E_0(aX + bA) + cX^2 + dXA + eA^2 = 0 \\ J &= 2: E_2^2 + E_2(pX + qA) + rX^2 + sXA + tA^2 = 0. \end{aligned} \tag{2}$$

Now for $X=0$, in the extreme (j,j) coupling the results must be

$$X = 0: E_0 = -3A \text{ and } +3A;\ E_2 = 0 \text{ and } -3A.$$

From this follows immediately for the coefficients:

$$b = 0,\ e = -9;\ q = 3,\ t = 0.$$

In the extreme Russell-Saunders coupling we consider first the finite roots.

$$X \text{ large:}\quad E_0 = +A;\ E_2 = -2A.$$

This gives

$$c = 0,\ d = -a;\ r = 0\ \ s = 2p.$$

The large roots in that case will be

$$E_0 = -aX;\ E_2 = -pX.$$

They represent the ${}^1S_0$ and the ${}^1D_2$. Now we need the result obtained by Slater in his above quoted paper, informing us that in the extreme Russell-Saunders coupling the order of the levels is as in our Fig. 1 and that the distance between ${}^3P$ and ${}^1S$ is 5/2 times that between ${}^3P$ and ${}^1D$. If we thus put $-p=2$, we must take $-a=5$ in order to agree with those results. The total set of expressions for p^4 thus becomes

$$\begin{aligned} J &= 1: E_1 = 0 \\ J &= 0: E_0^2 - 5XE_0 + 5XA - 9A^2 = 0 \\ J &= 2: E_2^2 - (2X - 3A)E_2 - 4XA = 0. \end{aligned} \tag{3}$$

For practical purposes it is easiest to choose A as the unit of energy as is done in Fig. 1. The figure shows the interesting crossing over of the triplet

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[7] In some cases the formulas become somewhat simpler if one chooses the center of gravity of a multiplet or of all the levels as reference level, but in practice it is easier to do it the way it is done here.

levels with $J=0$ and $J=1$. This explains for instance the partial inversion of this triplet as observed in tellurium.[8] With this same example we can check our expressions. The sum of observed E's for the levels with $J=0$ is $5X=-44+18441=18397$. For the levels with $J=2$ this sum is equal to $2X-3A$ and is observed to be $-4751+5808=1157$. It follows

$$X = 3680 \quad A = 2068, \quad X/A=1.78.$$

The energies calculated with these values are:[9]

$$\begin{array}{llll} J = 0 \text{ calc.} & -\ 13 & \text{obs.} & -\ 44 \\ & +\ 18410 & & +\ 18441 \\ J = 2 & -\ 4970 & & -\ 4751 \\ & +\ 6127 & & +\ 5808. \end{array}$$

Figure 2 represents the interval ratio of the triplet as a function of X/A. This figure may be usful to predict roughly the singlets if one knows the triplet in cases near the Russell-Saunders coupling. In such an extreme one may take for A one third of the observed total triplet. The triplet intervals must be known with accuracy however and it is therefore impossible to do this in the very important case of the oxygen spectrum. Assuming the interpretation of the auroral line to be correct, we can predict the position of the singlets with respect to the triplet and find (this time referred to the lowest level ${}^3P_0$):

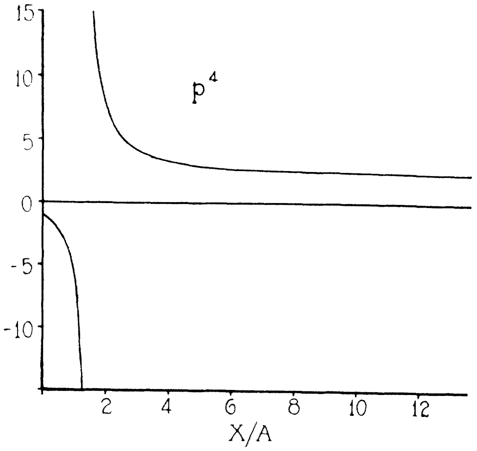

Fig. 2. Interval ratio for $p^4\ {}^3P$ for change from (j,j) to Russell-Saunders coupling.

$${}^1D_2 = 11984 \quad {}^1S_0 = 29909$$

which is very near the estimate of McLennan and Crawford.[10]

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[8] J. C. McLennan and M. F. Crawford, Nature **124,** 874 (1929).

[9] As was said above one can check the formulas in such a way as to make them come out either in good or rather bad agreement with the experiments. The way it is done here, however, is probably the least objectionable, being between the two.

[10] They give 10587 and 28512 which again proves that for predictions of this kind the intuition of an experienced spectroscopist is at least as good as any formula. Nature **124,** 874 (1929).

The configuration p^2. Figures 3 and 4 give the result for this configuration. As was to be expected it differs from p^4 only in the sign[11] of the coefficients of A. Here there is not such an interesting crossing over of levels as in the p^4 case. The total triplet distance is the same in both extreme couplings, but in between it is somewhat *larger*, which is the remarkable fact discovered by Sawyer and Humphreys.[12] It does not check, however, quantitatively.

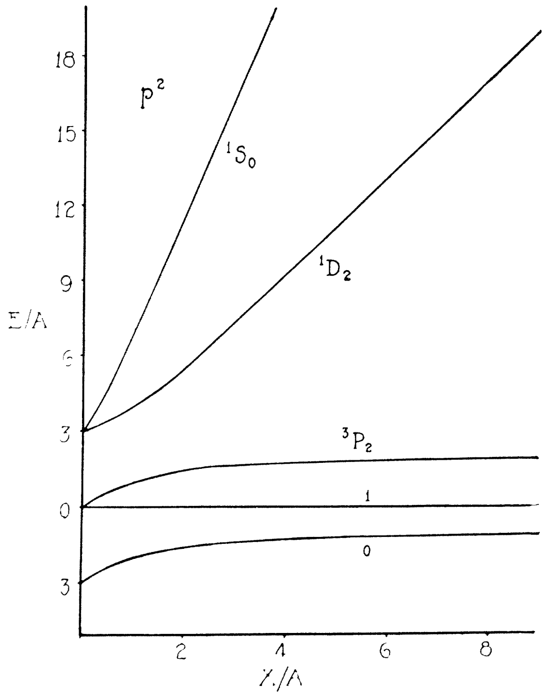

Fig. 3. Change in coupling for configuration p^2

We find a good fitting example in Sn I. By the same method used in the example for p^4 one obtains:

$J = 0$	calc.	-1633	obs.	-1692
		$+15412$		$+15471$
$J = 2$		$+1649$		$+1736$
		$+7008$		$+6921.$

The configuration p^3. This configuration gives one level with $J=2\frac{1}{2}$ one with $J=\frac{1}{2}$ and three with $J=1\frac{1}{2}$. In the extreme Russell-Saunders coupling they

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[11] It might perhaps have been better to take A negative in the case of p^4 and then the formulas for both cases would have been identical.

[12] R. A. Sawyer and C. J. Humphreys, Phys. Rev. **32,** 582 (1928). The explanation which I suggested at that time and which is mentioned in that article is now of course to be considered as pure nonsense.

form a ^4S, a ^2D and a ^2P, the first one being the lowest and from Slater's paper we obtain that their distances are in the ratio 3:2. From the theory of multiplet separations[5] we know that in the ideal case the ^2D and ^2P would show no multiplet splitting at all. For the extreme (j, j) coupling we find[13] a lowest level with $J=1\frac{1}{2}$, a distance $3A$ higher we find three levels with $J=\frac{1}{2}$, $1\frac{1}{2}$ and $2\frac{1}{2}$. Finally again $3A$ higher there is the third level with $J=1\frac{1}{2}$. We will choose the level with $J=2\frac{1}{2}$ as reference level. For the level with $J=\frac{1}{2}$ we expect a linear equation but for the three levels with $J=1\frac{1}{2}$ we must have a cubic equation. Writing down these equations with unknown coefficients gives us:

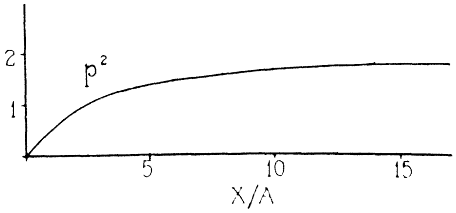

Fig. 4. Interval ratio of $p^2\ ^3P$ for different strengths of coupling.

$$\begin{aligned} J &= 2\tfrac{1}{2}: E_{2\frac{1}{2}} = 0 \\ J &= \tfrac{1}{2}\ : E_{\frac{1}{2}} = pX + qA \qquad\qquad (4) \\ J &= 1\tfrac{1}{2}: E_{1\frac{1}{2}}^3 + E_{1\frac{1}{2}}^2(aX + bA) + E_{1\frac{1}{2}}(cX^2 + dXA + eA^2) \\ &\qquad + fX^3 + gX^2A + hXA^2 + iA^3 = 0. \end{aligned}$$

It is easily found that the coefficient q for $E_{\frac{1}{2}}$ must be 0. With regard to Slater's result we will most conveniently choose $p=2$. For $J=1\frac{1}{2}$ we have the following known roots:

$$X = 0: \quad E_{1\frac{1}{2}} = -3A,\ 0,\ +3A.$$

$$X = \text{large}: \quad E_{1\frac{1}{2}} = -3X,\ 0,\ 2X, \text{ from Slater's results.}$$

This gives

$$i = 0, \quad b = 0, \quad e = -9;$$

$$f = 0, \quad a = 1, \quad c = -6.$$

We still can determine two more coefficients by remembering that the doublets in the extreme Russell-Saunders case must have zero separation. This means that their levels must fall together even if we take the first order terms of A into account for large X. From this it follows that

$$d = 0 \quad \text{and} \quad g = 0.$$

I see no way, however, to find the coefficient h by the method used here. The final equations are thus

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[13] Pauling and Goudsmit, reference 6, 256.

$$
\begin{aligned}
J &= 2\tfrac{1}{2}:\ E_{2\frac{1}{2}} = 0\\
J &= \tfrac{1}{2}\ :\ E_{\frac{1}{2}} = 2X\\
J &= 1\tfrac{1}{2}:\ E_{1\frac{1}{2}}{}^{3} + XE_{1\frac{1}{2}}{}^{2} - (6X^{2} + 9A^{2})E_{1\frac{1}{2}} + hXA^{2} = 0.
\end{aligned}
\tag{5}
$$

The first coefficients tell us that the sum of the levels with $J = 1\frac{1}{2}$ is half the distance of the level with $J = \frac{1}{2}$, all referred to $E_{2\frac{1}{2}}$. In As for instance we find $E_{\frac{1}{2}} = 7271 = 2X$ and the sum for $J = 1\frac{1}{2}$ is 3580 which indeed checks very well.[14] No good agreement can be found in Bi and in N, in the former case A and in the latter X is probably too large for a first order perturbation calculation to be sufficient.

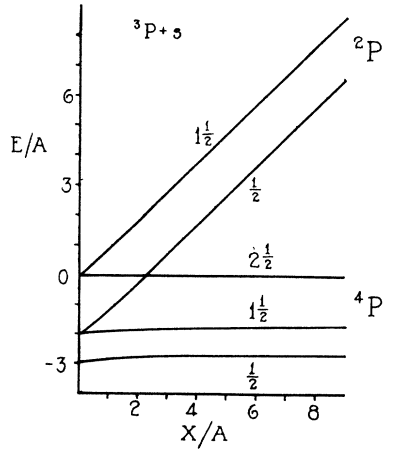

Fig. 5. Addition of an s-electron to a ^3P-state for different strengths of coupling.

The configuration ^3P+s and similar ones. It sometimes occurs that an electron is added to a very regular multiplet state of the next ion for which the connected multiplets of the same configuration are far away. Under such circumstances one may sometimes consider this multiplet as a state in itself and neglect the presence of the other states of the configuration. For such cases we can derive expressions for the variation of the levels with coupling, if we assume that the multiplet state to which the electron is added does not change at all. We will demonstrate this with the simplest example, a ^3P state with an added s-electron. In the extreme (j, j) coupling we find the triplet itself, slightly split up by the addition of the electron, as shown at the left of Figure 5. The total triplet separation we put equal to $3A$. In the extreme Russell-Saunders coupling we obtain a ^4P and a ^2P. The theory of multiplet separations[15] tells us that the separations in the quartet are $5/3\ A$ and A, and the doublet separation is $2A$. With the method described before one now finds, choosing the level with $J = 2\frac{1}{2}$ for reference, the following equations:

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[14] As the doublets in this example are small it proves Slater's relations rather than our formulas.

[15] For this case see S. Goudsmit and C. J. Humphreys, Phys. Rev. **31**, 960 (1928).

$$
\begin{aligned}
J &= 2\tfrac{1}{2}: E_{2\frac{1}{2}} = 0 \\
J &= 1\tfrac{1}{2}: E_{1\frac{1}{2}}^2 - (X - 2A)E_{1\frac{1}{2}} - 5/3AX = 0 \qquad (6)\\
J &= \tfrac{1}{2} : E_{\frac{1}{2}}^2 - (X - 5A)E_{\frac{1}{2}} - 8/3AX + 6A^2 = 0.
\end{aligned}
$$

Though these formulas may give the qualitative change very well, one can hardly expect a quantitative agreement except perhaps in a few extreme cases. Sb I is an example where the ^2P overlaps partially with the ^4P as shown in the left of Fig. 5.

It is not difficult to obtain the formulas for the addition of an s-electron to any multiplet, but if a p- or d- electron is added, it becomes much more complicated.

The configurations d^2 and d^8. As final examples in this paper we shall give the results for these configurations. They can be treated simultaneously and will differ in the sign of A, which will be positive for d^2 and negative for d^8. The levels arising from these configurations are

two with $J=4$
one with $J=3$
three with $J=2$
one with $J=1$
two with $J=0$.

We shall use the single level with $J=3$ as reference level. In the extreme Russell-Saunders coupling one finds ^3F, ^3P, ^1G, ^1D, ^1S. The distances of the centers of gravity of the various multiplets in the extreme Russell-Saunders coupling from the center of gravity of the ^3F, to which our reference level belongs, will be denoted by

$$
\begin{aligned}
{}^3F \text{ to } {}^3P &= \alpha X \\
{}^1G &= \beta X \\
{}^1D &= \gamma X \\
{}^1S &= \delta X.
\end{aligned}
$$

From Slater's results one obtains among the coefficients the following relations (for d^2 only):

$$
\begin{aligned}
\alpha &= 15 - 15t \\
\beta &= 12 + 2t \\
\gamma &= 5 + 9t \\
\delta &= 22 + 27t.
\end{aligned}
\qquad (7)
$$

In these expressions t is a new parameter, which from Slater's estimates is about 1/4. Slater showed for this configuration that the coupling energy depended upon two integrals, which will be different from case to case. These two integrals determine our coefficients. In d^8 and many other configurations more integrals enter combined in such a complicated way that no simple relations between the coefficients exist.

To determine as many coefficients as possible in our final formulas we must again take into account the first approximation in A for large X. This means that though the multiplets are far apart, we do not neglect their own splitting up, which, by the way, we know exactly from multiplet separation theory. We take the doublet separation for a single d-electron equal to $5A$. The total separation for the ^3F in the extreme Russell-Saunders coupling is then $7A$, and for the ^3P it is $3A$. Remembering that the distances expressed in X are between the centers of gravity one finds the following energies in the extreme cases:

$$\begin{array}{lll}
J = 3: & & E_3 = 0, \text{ reference level.} \\
J = 0: & X = 0: & E_0 = 5A, \; -5A \\
 & X \text{ large:} & \quad (\alpha X - A), \; (\delta X + A) \\
J = 1: & & E_1 = \alpha X \\
J = 2: & X = 0: & E_2 = 0, \; +5A, \; -5A \\
 & X \text{ large:} & \quad -3A, \; (\alpha X + 2A), \; (\gamma X + A) \\
J = 4: & X = 0: & E_4 = 0, \; +5A \\
 & X \text{ large:} & \quad +4A, \; (\beta X + A).
\end{array}$$

The following expressions are the final results. One sees again that one coefficient in the cubic equation for $J=2$ could not be determined by our method.

$$\begin{aligned}
&J = 3: E_3 = 0 \\
&J = 0: E_0^2 - (\alpha + \delta)XE_0 + \alpha\delta X^2 + (\alpha - \delta)XA - 25A^2 = 0 \\
&J = 1: E_1 = \alpha X \\
&J = 2: E_2^3 - (\alpha + \gamma)XE_2^2 + [\alpha\gamma X^2 - (2\alpha + \gamma)XA - 25A^2]E_2 \\
&\qquad\quad + 3\alpha\gamma X^2A + hXA^2 = 0 \\
&J = 4: E_4^2 - (\beta X + 5A)E_4 + 4\beta XA = 0
\end{aligned} \tag{9}$$

THE ZEEMAN EFFECT

The application of an external magnetic field may be treated by the addition of a perturbation parameter to our formulas. We denote the field strength by H, expressed in the right units so as to obtain wave numbers in our equations.[16] We then add terms with H to all our coefficients, but as we are only interested in the results for weak fields, we need consider the terms in the first power[17] of H only. We shall discuss the simple case in which the energy is given by a quadratic equation. One can easily extend it to more

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[16] For this purpose the wave-number shift of the normal Zeeman effect must be chosen as the unit.

[17] Taking into account all the powers of H would lead to the study of the Paschen-Back effect, which has been done in great detail by C. G. Darwin, Proc. Roy. Soc. **A115**, 1 (1927).

complicated cases but it is then in general impossible to determine all the necessary coefficients by our method. Equation (1) we will now write

$$E^2 + E(x + pH) + y_2 + qzH = 0. \tag{10}$$

In this equation x, y_2 and z stand symbolically for the linear and quadratic functions of the other perturbations, such as X and A. We assume that x and y_2 are completely known from the problem without field. The term in H^2 has been purposely omitted. We know that the field splits each level into a number of levels with different values of the magnetic quantum number M, but for our purpose we consider only an arbitrarily chosen value for this number. If E' and E'' were the energy levels without field, they become in the field

$$E = E' + Mg'H \text{ and } E'' + Mg''H.$$

Substituting these values in (10) leads at once to

$$g' = -\frac{pE' + qz}{2E' + x} \text{ and } g'' = -\frac{pE'' + qz}{2E'' + x}\cdot \tag{11}$$

There originally stood Mg' and Mg'', but just because M enters here merely as a proportionality factor we can put it equal to 1 irrespective of the fact whether this is an in reality possible value for M or not. From the first part of this paper we have

$$x = -E' - E''.$$

Substituting this and adding the two g-values shows

$$g' + g'' = -p. \tag{12}$$

This is the well-known g-sum rule for this simple case and it tells us at once the value of the coefficient p. The coefficients q of the linear function z of the other perturbation parameters has not such a simple meaning but can always be found by means of the known g-values in extreme couplings.

In our example of the configuration p^4 we find for instance

$$\text{for } J = 2 \qquad g = \frac{5/2E - 3X + 7/2A}{2E - 2X + 3A} = \frac{5/2E' - 3X + 7/2A}{E' - E''}\cdot \tag{13}$$

For p^2 one obtains again the same formulas but with the sign of A reversed.

CONCLUSION

We have illustrated our method of deriving relations between multiplets by various examples. Needless to say it is possible to apply it to many more cases than have been mentioned here. For instance it is clear that the formulas derived by Houston can be easily obtained by our method.

In a following paper a few more cases will be treated and the formulas will be applied to the available spectroscopic material. It is actually surprising that in many instances they are not so very bad after all and even the discrepancies may prove to be of interest.[18]

The intensities can be treated by a similar procedure as used in this paper especially since we now know the intensity formulas for the extreme (j, j) coupling from the recent paper by Bartlett.[19]

This and the following paper, I hope, will contribute a little bit to the understanding of spectra with intermediate coupling. The fact that so few of such spectra have been analysed at present is certainly only due to a lack of theoretical knowledge of their structure, for the classification of these spectra can not be so very much harder than for multiplet spectra. But one must not look for multiplets in spectra where there are not such structures and one perhaps ought to start by abolishing the use of multiplet notations in those cases, where they are, in the main, meaningless and misleading.

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[18] Compare a paper by Laporte and Inglis treating important examples of the d^9s and p^5s configurations, as was mentioned at the beginning of this article. This issue, p. 1337.

[19] J. H. Bartlett, Phys. Rev. **35**, 229 (1930).