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ZEEMAN EFFECT IN INTERMEDIATE COUPLING

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Abstract

A method is given for calculating g-values in intermediate coupling when the matrix of internal energy of the atom (spin-orbit plus electrostatic interaction) is known in LS coupling. The transformation from the states of LS coupling to the states of intermediate coupling, in which the internal energy matrix is diagonal, is then readily determined in terms of the parameters expressing the relative magnitudes of the interactions. The coupling parameters are ascertained from the measured energy levels. The transformation so determined is applied to the matrix of the energy due to an external magnetic field, as known for LS coupling. The diagonal terms of the transformed matrix contain the g-values of the states of the atom in intermediate coupling. Application of the method is made to the configurations p^2, p^3 and d^2. Agreement with the available experimental g-values is satisfactory, being as good as the agreement of energy levels to be had from a first order calculation.

THE "anomalous" Zeeman effect for two-electron configurations with one s-electron has been treated by Houston.[1] Goudsmit[2] has extended the treatment to another special type of configuration, p^2 and p^4. The energy level problem for general two-electron configurations has been treated in the preceding paper in a manner which makes possible an easy method for calculating g-values in intermediate coupling. The method applies to any atom of which the matrix of the perturbing energy of the electrons is known in LS coupling.

Zeeman effect (as distinguished from Paschen-Back effect) is concerned with an external magnetic field sufficiently weak that the magnitude of the total angular momentum is a constant of the motion. Then the components of the energy matrix between states of different values of J may be neglected. In LS coupling L^2, S^2 and J_z are diagonal matrices (being constants of the motion), and they commute with L_z and S_z. Thus the energy due to the external field, $(L_z+2S_z)H$, has matrix elements only between states with the same quantum numbers L, S and M_J. As we neglect the elements between states of different J value, this Zeeman energy is a diagonal matrix in LS coupling. From Eqs. (3), (4) and (5) of the preceding paper, we have the familiar result

$$\begin{aligned} H(L_z+2S_z)^{LSJMJ}_{LSJM_J} &= HM_J(L^{LSJ}_{LSJ}+2S^{LSJ}_{LSJ}) \\ &= HM_J\frac{3J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \qquad (1) \\ &= HM_J g_{LSJ} \end{aligned}$$

giving the Landé g-values in LS coupling.

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

[2] S. Goudsmit, Phys. Rev. **35**, 1325 (1930).

If we know the matrix of the internal energy of the atom in LS coupling, we can find the transformation, R, which carries it to diagonal form. R will have no components between states of different J and M_J, as the internal energy commutes with J^2 and J_z. Hence it is sufficient to consider together states with the same J and M_J.

The matrix of the energy due to the external field is diagonal in LS coupling, and has the elements HM_Jg_k, where g_k is the g-value of a state specified by the quantum numbers $L_kS_kJ_k$. This matrix may be transformed to intermediate coupling:

$$HM_Jg' = HM_JRgR^{-1}.$$

We treat the energy due to the external field as a perturbation of the atom in intermediate coupling, expanding in powers of the perturbation parameter H. The first order corrections to the energies are the diagonal elements of the perturbing energy matrix. The g-values are defined by the coefficients of the first power of H in the energies,[3] so they are the diagonal terms

$$g_k' = \sum_l R(kl)g_lR^{-1}(lk) = \sum_l R(kl)g_lR^*(kl). \qquad (2)$$

APPLICATIONS

The configuration p^2. Here the levels with $J=0$ are not split up by the field and the level with $J=1$, ${}^3P_1$, has $g=3/2$ for all couplings. For the levels with $J=2$ the matrix of the g-values in LS coupling is

$$\begin{array}{c|cc} & {}^1D_2 & {}^3P_2 \\ \hline {}^1D_2 & 1 & 0 \\ {}^3P_2 & 0 & 3/2 \end{array}$$

Using the energy matrix from the preceding paper (with ${}^3P_1$ as reference level), we find for the transformation matrix,

$$R(k1) = \frac{2^{1/2}(\epsilon_k - 1)}{[2(\epsilon_k - 1)^2 + 1]^{1/2}}$$

$$R(k2) = \frac{1}{[2(\epsilon_k - 1)^2 + 1]^{1/2}}.$$

In these equations $\epsilon_k = W_k/a$, where W_k is the energy of a state in intermediate coupling (a solution of the secular equation for $J=2$ in the preceding paper) and a is the parameter of spin-orbit interaction. We find for the g-values in intermediate coupling[4]

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[3] The g-values are thus independent of the nondiagonal elements of the transformed matrix, and therefore small elements of the matrix that are nondiagonal with respect to J^2 in LS coupling do not affect the g-values.

[4] With Goudsmit's method,[2] which applies especially to this case, we obtain the formula

$$g_k' = \frac{5}{4} + \frac{1/4 - X/a}{2(\epsilon_k - \epsilon_e)}$$

$$g_k' = \frac{2(\epsilon_k - 1)^2 + 3/2}{2(\epsilon_k - 1)^2 + 1}\,.$$

This formula has been applied in calculating the values listed in Table I. The parameters have been determined simply from their relations to the energy sums. The energy values calculated from these parameters are also listed, and are seen to agree with the observed levels as well as is to be expected from a first order calculation.

TABLE I. *Energies and g-values of the configuration p^2.*

	Sn I $5p^2$					Pb I $6p^2$				
	$J=0$	2	2	1	0	$J=0$	2	2	1	0
ν obs.	15471	6921	1736	0	−1692	21639	13639	2831	0	−7817
ϵ_k obs.	7.39	3.31	0.83	0	−0.81	2.96	1.87	0.39	0	−1.07
ϵ_k calc.	7.34	3.35	0.78	0	−0.76	2.97	1.85	0.41	0	−1.08
g (LS)		1.00	1.50	1.50			1.00	1.50	1.50	
g_k' calc.		1.042	1.458	1.50			1.205	1.295	1.50	
g_k' obs.*		1.050	1.420	1.501			1.230	1.269	1.501	

* E. Back, Zeits. f. Physik **43,** 309 (1927). The g-values for Sn I observed by Green and Loring (Phys. Rev. **30,** 574, 1927) agree with Back's, except that they have 1.46 instead of 1.420, in better agreement with the theoretical value and with the g-sum rule.

The configuration p^3. For this case the multiplets are ^2D, ^2P, and ^4S. The g-values for $^2D_{5/2}$ and $^2P_{1/2}$ are independent of the coupling. For the levels with $J=3/2$ the equation for the energies has been given by one of us[5] as

$$W^3 + W^2X - W(9a^2/4 + 6X^2) - 15Xa^2/4 = 0.$$

The energies of the states in LS coupling are known, and contain no term in the first power of a. This and the selection rule that $\Delta L = 0, \pm 1$ and $\Delta S = 0, \pm 1$ for the matrix components of the spin-orbit interaction limit the energy matrix to the form

$$\begin{array}{c|ccc} & {}^2D_{3/2} & {}^2P_{3/2} & {}^4S_{3/2} \\ \hline {}^2D_{3/2} & 0 & \alpha_1 & 0 \\ {}^2P_{3/2} & \alpha_1 & 2X & \alpha_2 \\ {}^4S_{3/2} & 0 & \alpha_2 & -3X \end{array}$$

with $^2D_{5/2}$ taken as reference level. This yields the secular equation

$$W^3 + W^2X - W(\alpha_1^2 + \alpha_2^2 + 6X^2) - 3X\alpha_1^2 = 0.$$

(his equation 13). Application of this formula also gives the results of Table I. It differs from ours in form, since his method is a solution of a secular equation directly for energies, and involves no transformation coefficients. It is equivalent to solving the equation

$$\begin{vmatrix} e_{11} + g_1H - \epsilon_0 - g'H & e_{12} \\ e_{21} & e_{22} + g_0H - \epsilon_0 - g'H \end{vmatrix} = 0$$

where the terms without H vanish, ϵ_0 being a solution for zero field. When we go to determinants of higher order, the coefficient of H involves nondiagonal elements. A direct solution of the determinant becomes increasingly unwieldy, and Goudsmit's method fails with too few relations to determine the coefficients.

[5] D. R. Inglis, Phys. Rev. **38,** 377 (1931).

Comparison with the above determines[6]

$$\alpha_1^2 = 5a^2/4$$
$$\alpha_2^2 = a^2$$

For the transformation matrix we find

$$R(k1) = \frac{5^{1/2}}{2}\,\frac{\epsilon_k + 3X/a}{\epsilon_k}\,R(k3)$$
$$R(k2) = (\epsilon_k + 3X/a)R(k3)$$
$$R(k3) = \frac{1}{[1 + (5/4\epsilon_k + 1)(\epsilon_k + 3X/a)]^{1/2}}\,.$$

In *LS* coupling

$$g = \begin{array}{c|ccc} & {}^2D_{3/2} & {}^2P_{3/2} & {}^4S_{3/2} \\ \hline {}^2D_{3/2} & 4/5 & 0 & 0 \\ {}^2P_{3/2} & 0 & 4/3 & 0 \\ {}^4S_{3/2} & 0 & 0 & 2 \end{array}$$

Hence for the *g*-values in intermediate coupling we have

$$g_k' = \frac{\epsilon_k^2 + (4\epsilon_k^2/3 + 1)(\epsilon_k + 3X/a)}{\epsilon_k^2 + (\epsilon_k^2 + 5)(\epsilon_k + 3X/a)}\,.$$

The comparison with experimental data[7] is indicated in Table II.

TABLE II. *Energies and g-values of Bi I, $6p^3$.*

	$J=1\frac{1}{2}$	$\frac{1}{2}$	$2\frac{1}{2}$	$1\frac{1}{2}$	$1\frac{1}{2}$
ν obs.	17728	6223	0	−4018	−15437
ϵ_k obs.	1.81	0.637	0	−0.41	−1.58
ϵ_k calc.[5]	1.73	0.637	0	−0.44	−1.62
g (*LS*)	4/3	2/3	6/5	4/5	2
g_k' calc.	1.25			1.25	1.66
g_k' obs.	(1.26)			1.225	1.65*

* A tentative value kindly communicated to us by R. F. Bacher. The other measured value is taken from his dissertation (Michigan, 1930). The value in parentheses is known only from the measurements of the others through the sum rule.

The configuration d^2. In this case the levels with $J=4$ and with $J=2$ are of interest. For the levels with $J=4$, we find the following transformation matrix when the energy matrix of the preceding paper is used and ${}^3F_3$ is taken as reference level:

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[6] A similar determination is possible in other very simple cases where we know the secular equation from consideration of extreme couplings. In these few cases we are not dependent upon the preceding paper, or the method of Gray and Wills, for the energy matrix.

[7] The only further measurements of "anomalous" *g*-values for interesting configurations of which we are aware are for Ne I, $2p^53p$. Here the magnetic parameters may be estimated from the doublet separations of Ne II and Na I, but we have found no satisfactory fit for the energies, so no *g*-values could be calculated.

$$R(k1)=\frac{\epsilon_k-2}{[(\epsilon_k-2)^2+1]^{1/2}}\qquad R(k2)=\frac{1}{[(\epsilon_k-2)^2+1]^{1/2}}$$

In *LS* coupling we have

$$g=\begin{array}{c|cc} & {}^1G_4 & {}^3F_4 \\ \hline {}^1G_4 & 1 & 0 \\ {}^3F_4 & 0 & 5/4 \end{array}$$

Then, in intermediate coupling,

$$g_k'=\frac{(\epsilon_k-2)^2+5/4}{(\epsilon_k-2)^2+1}\,.$$

For the levels with $J=2$ the transformation coefficients are

$$R(k1)=-\frac{2(3/5)^{1/2}}{\epsilon_k+3/2}R(k2)$$

$$R(k2)=\left[\frac{12}{5(\epsilon_k+3/2)^2}+\frac{21}{10(\epsilon_k-\gamma/a-1)^2}+1\right]^{-1/2}$$

$$R(k3)=\frac{(21/10)^{1/2}}{\epsilon_k-\gamma/a-1}R(k2)$$

where $\gamma=(15/49)F^2-(75/441)F^4$. From the matrix

$$g=\begin{array}{c|ccc} & {}^3F_2 & {}^1D_2 & {}^3P_2 \\ \hline {}^3F_2 & 2/3 & 0 & 0 \\ {}^1D_2 & 0 & 1 & 0 \\ {}^3P_2 & 0 & 0 & 3/2 \end{array}$$

we get the g-values in intermediate coupling,

$$g_k'=\frac{\{32+20(\epsilon_k+3/2)^2\}(\epsilon_k-\gamma/a-1)^2+63(\epsilon_k+3/2)^2}{\{48+20(\epsilon_k+3/2)^2\}(\epsilon_k-\gamma/a-1)^2+42(\epsilon_k+3/2)^2}\,.$$

CONCLUSION

The agreement of calculated Zeeman effect with experiment, judged by percentage discrepancy, is usually[8] considerably better than the agreement of observed and calculated energy levels, after adjustment of the radial-integral parameters. In judging calculations of g-values, however, one must bear in mind that they vary between quite narrow limits while the parameters of energy vary all the way from the parameters of *LS* to those of *(jj)* coupling. A fairer criterion of agreement of an intermediate-coupling g-value is then the relative error in the deviation from the extreme-coupling g-value. One cannot expect greater accuracy in the calculation of g-values than in the

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[8] See also reference 1; Laporte and Inglis, Phys. Rev. **35,** 1337 (1930); J. Bakker, Naturwiss., **18,** 1100 (1930).

calculation of energy separations in a first-order treatment of this sort. A disagreement of energy levels with theoretical values causes a maladjustment of parameters, which makes an error in the g-value calculated in terms of the parameters. In addition, there are errors due to second-order contributions of the states of other configurations to the g-values directly. In Tables I and II, the agreement of the g-values with experiment is entirely satisfactory.

Application of the method has here been made to only a few of the simplest cases.[9] Calculation of g-values of other two-electron configurations should be of interest with extension of the experimental data. For more than two electrons, the calculations are also possible, but are limited by the difficulty in determining the energy matrix for configurations in which the same multiplet appears more than once.

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[9] *Footnote added in proof, October 14*: Calculations for p^2 by the method of Goudsmit, corresponding to and agreeing with Table I, are given by Green and Loring (Phys. Rev. in print). In the preparation of Table II, the magnetic data for Sb I (H. Löwenthal, Zeits. f. Physik **57**, 828 (1929); Green and Loring, Phys. Rev. **31**, 707 (1928) were overlooked. They agree satisfactorily with the theory:

TABLE II, *A. g-values of Sb I, 5*p^3.

J	$1\frac{1}{2}$	$\frac{1}{2}$	$2\frac{1}{2}$	$1\frac{1}{2}$	$1\frac{1}{2}$
ϵ_k obs.	2.72	1.86	0	−0.38	−2.79
ϵ_k calc.	2.51	1.86	0	−0.46	−3.02
g_k calc.	1.267	2/3	6/5	0.908	1.955
g_k obs.	1.280	0.668	1.205	0.898	1.967

For this configuration, $a=3520$, $X=3270$. For As I, $4p^3$, which is near (LS) coupling, the predicted g-values are 1.319, 2/3, 6/5, 0.825, and 1.988.

It has been remarked (Green and Loring, Phys. Rev. in print; L. A. Young, W. V. Houston, in conversation) that much of the disagreement between theoretical and experimental energy levels may be due to our neglect in the Hamiltonian of those terms corresponding to coupling of the spin of one electron to the orbit of the other, and to spin-spin interaction, which assume importance in the triplets of He and Li^+. These neglected terms become relatively small linearly with increasing *effective* nuclear charge. They are thus expected to be smaller for the configurations p^5s and d^9s than for ps, ds, p^5p, etc. It has been apparent (reference 8) that the agreement is indeed more satisfactory in the former cases, provided there be no overlapping of configurations.