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Changes in g-Values, in a Spectrum, for Different Magnetic Fields

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Based on the theory of the partial Paschen-Back effect a quantitative explanation is given of the fact, recently discovered by the authors, that an atomic energy level of Mn I, namely $z\,^6F^\circ_{1\frac{1}{2}}$, has two different values for the Landé splitting-factor g: one for each pair of the magnetic levels $M=\pm 1\frac{1}{2}$ and $\pm 0\frac{1}{2}$.

Attention is called to the fact that g-values, in cases such as those observed in Mn I, experience important alterations when the magnetic field is increased from about 40,000 oersteds, which is the magnitude of fields used in the past, to about 80,000, as actually used in observing Zeeman patterns at M.I.T. for the purpose of analyzing spectra.

It is pointed out that if g-values accompany a list of term-designations and term-values, it is desirable to specify the magnitude of the magnetic field to verify the correctness of the designations given in the analysis of the spectrum. Otherwise any alterations which the g-values may undergo will not be correctly interpreted.

RECENTLY[1] the authors have given an interesting case of an atomic energy state of the manganese atom, that of the level $z\,^6F_{1\frac{1}{2}}$, whose two pairs of magnetic levels, $M=\pm 1\frac{1}{2}$ and $M=\pm 0\frac{1}{2}$, have different g-values: 1.067 and 1.003, respectively.

The observed variation of g-values was tentatively ascribed to displacements which the magnetic levels experience owing to the proximity of other levels with the same M belonging to $z\,^6F_{0\frac{1}{2}}$. The hypothesis was based on the observed fact that the change in g-value in $z\,^6F_{1\frac{1}{2}}^{\pm 0\frac{1}{2}}$ was equal, and of contrary sign, to that observed in $z\,^6F_{0\frac{1}{2}}^{\pm 0\frac{1}{2}}$.

We are now in a position to prove this hypothesis quantitatively and, at the same time, to give the reasons that have concurred in this particular case to make the change in g-value so evident.

In the theory of the partial Paschen-Back effect[2] the magnitude of the displacement of a magnetic level, due to the interaction with another level of the same M-value, and belonging to each of two consecutive levels of the same spectral term, is given by

$$\epsilon = I^2/\delta. \tag{1}$$

In this equation ϵ represents the displacement, δ is the distance between the two repelling levels, and I is the *interaction factor* as given by Eq. (2). The three magnitudes are given in Lorentz units.

$$I=\left[\frac{(J-L+S)(J+L-S)(L+S+1+J)(L+S+1-J)}{4J^2(2J-1)(2J+1)}\right]^{\frac{1}{2}}(J^2-M^2)^{\frac{1}{2}}. \tag{2}$$

Equation (2) shows that I is a function of M^2, which means that the I-values are not affected by the sign of M. The same displacements are expected, in magnitude and sign, in two sub-levels $-M$ and $+M$ of the same atomic levels. Owing to this fact, the magnetic components of the same order, on each side of the central line in a pattern, show the same displacements and in the same sense, thus keeping their distances unperturbed. In calculating g-values it is the usual practice to take advantage of these circumstances to eliminate distortions due to partial Paschen-Back effect.

This general procedure of determining g-values will give serious errors in such cases as that of Mn I considered here. For a better understanding of this we have selected an arbitrary example. Two atomic levels $T_{1\frac{1}{2}}$ and $T_{0\frac{1}{2}}$ (consecutive in the same term T) and their magnetic levels $M=\pm 0\frac{1}{2}$ are given in Fig. 1. The distance between the two atomic levels is δ and those between the magnetic levels are $g_{1\frac{1}{2}}$ and $g_{0\frac{1}{2}}$. These separations represent the corresponding g-values. We have selected $g_{1\frac{1}{2}}>g_{0\frac{1}{2}}$. The distance between the two negative magnetic levels is indicated by δ^- and that between the positive by δ^+.

If we first suppose that δ is large compared with $g_{1\frac{1}{2}}$ and $g_{0\frac{1}{2}}$ (this is not the case of Fig. 1), the distances δ^- and δ^+ can be taken equal to δ. The same approximation can be made, though δ is not large, if $g_{1\frac{1}{2}}$ and $g_{0\frac{1}{2}}$ do not differ much.

In these very usual cases Eq. (1) will give equal displacements ϵ for levels $-M$ and $+M$ (of the same

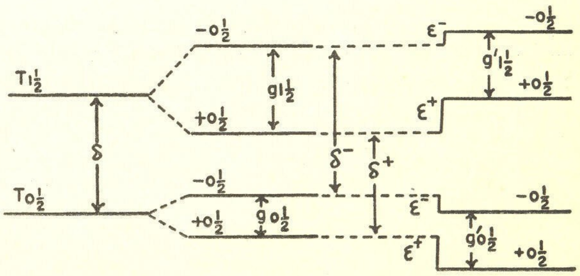

FIG. 1. Shift of magnetic levels due to Paschen-Back interaction.

[1] M. A. Catalán and R. Velasco, Proc. Roy. Soc. **A63**, 917 (1950).

[2] C. C. Kiess and G. Shortley, J. Research Nat. Bur. Stand. **42**, 183 (1949).

TABLE I.

Atomic level	M	$M\cdot a\cdot g$	e	$e+M\cdot a\cdot g$	$ag'(\mathrm{cm}^{-1})$	g'(L.U.)
$z\,^6F_{1\frac{1}{2}}$	$-0\frac{1}{2}$	-2.11	-1.09	-3.20	3.92	0.990
	$0\frac{1}{2}$	2.11	-1.39	0.72		
$z\,^6F_{0\frac{1}{2}}$	$-0\frac{1}{2}$	1.32	1.09	2.41	-2.34	-0.591
	$0\frac{1}{2}$	-1.32	1.39	0.07		

atomic level). I being the same, and the distances also being the same for $-M$ as for $+M$, the resulting ϵ^- and ϵ^+ must be equal. In such cases the ordinary methods of determining g-values will give accurate results.

But in cases, such as that represented in Fig. 1, with a *large difference between the g-values* $g_{1\frac{1}{2}}$ *and* $g_{0\frac{1}{2}}$, the distances δ^- and δ^+ are no longer equal. Equation (1) when applied to pairs of levels with unequal distances, in spite of the equality of I-values, will give different ϵ-values: ϵ^- will be smaller than ϵ^+.

In Fig. 1 the perturbations ϵ^- and ϵ^+ are applied to the magnetic levels from $T_{1\frac{1}{2}}$ in an opposite direction to those from $T_{0\frac{1}{2}}$. The resulting perturbing levels are separated by new values $g'_{1\frac{1}{2}}$ and $g'_{0\frac{1}{2}}$.

If the new separations, the new g-values, are compared with the old ones, it will be seen that $g_{1\frac{1}{2}}$ has been decreased by the same amount as $g_{0\frac{1}{2}}$ is increased. The *g-values have both been altered*, but their sum remains unaltered.

We are now prepared to consider quantitatively the case of levels $z\,^6F_{1\frac{1}{2}}$ and $z\,^6F_{0\frac{1}{2}}$ of Mn I. Here we have two pairs of interacting levels: $z\,^6F_{1\frac{1}{2}}^{-0\frac{1}{2}}$, $z\,^6F_{0\frac{1}{2}}^{-0\frac{1}{2}}$ and $z\,^6F_{1\frac{1}{2}}^{+0\frac{1}{2}}$, $z\,^6F_{0\frac{1}{2}}^{+0\frac{1}{2}}$. The Landé g-values for levels $^6F_{1\frac{1}{2}}$ and $^6F_{0\frac{1}{2}}$ are 1.067 and -0.667, respectively. The difference between these values, 1.733, being very great, makes this case analogous to the arbitrary one explained above.

For simplicity in the comparison with the experimental results we shall use cm^{-1} in this case instead of Lorentz units. Equation (1) for the interaction measured in cm^{-1} can be written

$$e=I^2a^2/d, \tag{3}$$

where e and d are the displacement and the distance between levels, in cm^{-1}. As I-values from Eq. (2) are in L.U., it is necessary to multiply them by the value a of the *normal separation.*

TABLE II.

	Calculated	Observed
$z\,^6F_{1\frac{1}{2}}^{\pm 0\frac{1}{2}}$	0.990	1.003
$z\,^6F_{0\frac{1}{2}}^{\pm 0\frac{1}{2}}$	-0.591	-0.598
Sum	0.399	0.405

TABLE III.

Atomic level	M	$M\cdot a\cdot g$	e	$e+M\cdot a\cdot g$	$ag'(\mathrm{cm}^{-1})$	g'(L.U.)
$z\,^6F_{1\frac{1}{2}}$	$-0\frac{1}{2}$	-1.06	-0.29	-1.35	2.09	1.056
	$0\frac{1}{2}$	1.06	-0.32	0.74		
$z\,^6F_{0\frac{1}{2}}$	$-0\frac{1}{2}$	0.66	0.29	0.95	-1.29	-0.652
	$0\frac{1}{2}$	-0.66	0.32	-0.34		

The distance between the two atomic levels involved is $d=28.51\ \mathrm{cm}^{-1}$. The separations d^- and d^+ (see Fig. 1) can be calculated by Eqs. (4)

$$\begin{aligned} d^- &= d+\tfrac{1}{2}ag_{1\frac{1}{2}}-\tfrac{1}{2}ag_{0\frac{1}{2}} \\ d^+ &= d-\tfrac{1}{2}ag_{1\frac{1}{2}}+\tfrac{1}{2}ag_{0\frac{1}{2}}. \end{aligned} \tag{4}$$

The g-values, which are in L.U., have been multiplied by a in formulas (4).

The value of a for this experimental case, in which the magnetic field was 85,040 oersteds, is 3.96. Thus we shall have:

$$\begin{aligned} d^- &= 28.51+1.98\times1.067-1.98\times(-0.667) \\ &= 28.51+2.11+1.32=31.94\ \mathrm{cm}^{-1}. \\ d^+ &= 28.51-1.98\times1.067+1.98\times(-0.667) \\ &= 28.51-2.11-1.32=25.08\ \mathrm{cm}^{-1}. \end{aligned} \tag{5}$$

The large difference existing between the two distances d^- and d^+ should be noted; we expect therefore very different e-values in the two cases.

In a paper on asymmetrical patterns Catalán[3] gives a table with the different possible values for I. For levels $^6F_{1\frac{1}{2}}^{\pm 0\frac{1}{2}}$ the value $I^2=2.22$ is given. With this value and those of d^- and d^+, taken from Eq. (5), Eq. (3) gives the values found in Table I.

The perturbed g'-values here obtained are in close agreement with those obtained by experiment, as described in reference 1, in spite of the fact that formula (1) is only a rough approximation. This is shown in Table II.

Evidently the g-values computed *for different fields* will not be equal in cases such as that of $z\,^6F$ of Mn I. The calculated values for this case with a field of 42,520 (half of the value used before) are found in Table III. A comparison of the resulting values for the two

TABLE IV. Magnetic field (in oersteds).

	Very weak	42520	85040
$z\,^6F_{1\frac{1}{2}}^{\pm 1\frac{1}{2}}$	1.067	1.067	1.067
$z\,^6F_{1\frac{1}{2}}^{\pm 0\frac{1}{2}}$	1.067	1.056	0.990
$z\,^6F_{0\frac{1}{2}}^{\pm 0\frac{1}{2}}$	-0.667	-0.652	-0.591

[3] M. A. Catalán, J. Research Nat. Bur. Stand. (to be published).

different fields, and for a very weak field (Landé value), is given in Table IV.

This comparison clearly shows that, though the changes in g-values on passing from a very weak field to one of about 40,000 oersteds are unimportant, if this value of the field is doubled then the change may, at least in some cases, be of great magnitude.

When one considers that most tables with accurate g-values, published in recent years, have been derived from plates taken at M.I.T., with fields of more than 80,000 oersteds, one is justified in thinking that many of the g-values in such tables may have been altered by interactions. Only by specifying clearly the field used in the observations can such tables have an accurate meaning.

Furthermore, in some extreme cases such as that of $z\,^6F_{1\frac{1}{2}}$ of Mn I, it will be necessary to give separately the g-values for the different magnetic levels. Otherwise what "mean" value can be deduced for an atomic level $z\,^6F_{1\frac{1}{2}}$ of manganese whose two pairs of magnetic levels have, respectively, the g-values 1.067 (for $M=\pm 1\frac{1}{2}$) and 1.003 (for $M=\pm 0\frac{1}{2}$)?