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Asymmetries of Zeeman Patterns and g-Values for Neutral Manganese

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Spectrograms of manganese made at the Massachusetts Institute of Technology with fields in excess of 84,000 oersteds show many lines that exhibit various degrees of distortion in both the positions and the intensities of the magnetic components. The interpretation of these asymmetric patterns has been made by the approximate theory of the partial Paschen-Back effect. The g-values that have been derived for several energy levels of Mn I are found to conform, in most cases, with those required for LS-coupling. A few exceptions to this rule have been considered in some detail. General tables have been computed, which will permit explanation of the distortions in other spectra. will permit explanation of the distortions in other spectra.

1. Introduction

Ever since the discovery of the splitting of spectral lines by a magnetic field (Zeeman effect) the observers have called attention to the fact that some of the patterns are asymmetrical, the distances between their magnetic components being not rigorously equal. These asymmetries make it difficult to compute the g-factors that govern the splitting. Two early examples of asymmetric patterns are given by Martinez Risco [1],3 and by Back and Landé [2].

At that time it was impossible to determine which of these different separations between magnetic components ought to be used as coefficients in the equations for obtaining the g-values of the atomic levels. Back adopted an empirical procedure, which is described in his paper on manganese [3]. This procedure has since been much used because in many cases it gives values in complete agreement with the LS-coupling values.

In recent years some authors, who have had the opportunity of measuring the beautiful plates made at the Massachusetts Institute of Technology by Harrison and his collaborators using magnetic fields of about 85,000 oersteds, have again called attention to the fact that some of the patterns are

very asymmetrical [4].

The author of this paper, who is at present working on the structure of the manganese spectrum, has measured some excellent plates made at MIT in 1939. The measurements indicate that many of the patterns are more or less asymmetrical, and that these asymmetries affect the g-values by as much as a few percent depending on the rules adopted to calculate the average separation between components. On these plates many of the most interesting asymmetric lines appear too weak to be measured accurately, some of the faint components being absent in many cases. It was, therefore, decided to obtain new, long-exposure spectrograms of the manganese spectrum in the magnetic field.

The large Bitter magnet of the MIT, which had not been in operation since the war, was again put to work (not, however, without considerable trouble) by J. C. van den Bosch and the writer with the help of G. R. Harrison's assistants. A beautiful set of plates in which the interesting asymmetric patterns appear strongly was then secured. The procedure employed in making the spectrograms is that described by Harrison and his collaborators [5].

The electrodes for these plates were prepared by compressing powdered manganese with silver dust. The manganese was prepared by an electrolytic process and presented to us by W. F. Meggers. It

was extremely pure.

The accurate measurements of these spectrograms by the author have permitted him to ascertain the cause of the observed asymmetries and at the same time to deduce the best procedure to eliminate the distortion in the computation of g-values. These distortions in the magnetic patterns appear in both the positions and the intensities of the components. In the following we shall describe first the asymmetries of the positions and later we shall consider the perturbations in the intensities.

2. Experimental Asymmetrical Patterns

The pattern for the line $a^6\mathrm{D}_{1\frac{1}{2}}-z^6\mathrm{D}_{2\frac{1}{2}}^\circ=24485.25$ cm⁻¹ of Mn I, at 4082.945 A, obtained experimentally shows *unequally spaced* components. Irregular intervals between adjacent components are found both in the π - and σ -components. This is an example of an asymmetrical pattern, which contrasts with the symmetrical ones generally described. In table 1 the theoretical values of the wave numbers of the components are compared with the observed values [6] for this line. The experimental intervals, although irregular, show curious regularities. Any cause to which the asymmetry of the pattern may reasonably be ascribed will not alter the validity of the combination principle. This means that the displacements observed in the magnetic lines will be due to displacements of the magnetic levels involved. A perturbed level will show the same displacement in all lines that originate in it. Double-array tables will then be suitable to represent an asymmetrical pattern, and in such tables the magnetic levels will appear with their displacements.

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³ Figures in brackets indicate the literature references at the end of this paper.

Table 1. Theoretical and observed components of 24485.25 cm⁻¹ of Mni [Lorentz Unit a=3.955 cm⁻¹]

Polarization	Theoretical unperturbed wave number, ν	Interval, $\Delta \nu$	Observed perturbed wave number, ν	Interval, Δ
σ	_ 24477. 45	0.00	24477. 18	
σ	24478. 28	0. 83	24478. 32	1. 14
σ	24479. 11	0. 83	24479. 21	0.89
σ	_ 24479. 95	0. 84	24479. 88	0. 67
$\pi_{}$	24484. 00	0.04	24483, 83	
π	24484. 84	0. 84	24484. 88	1. 05
π	24485. 66	0. 82	24485. 72	0. 84
$\pi_{}$	24486. 50	0.84	24486. 32	0. 60
σ	24490. 55	0.04	24490. 49	
т	24491. 39	0. 84	24491. 49	1. 00
T	24492. 22	0. 83	24492. 23	0. 74
T	24493, 05	0.83	24492. 84	0. 61

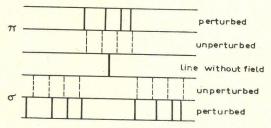


Figure 1. Comparison of positions of components in a perturbed and an unperturbed pattern.

In a perturbed pattern either the π - or the σ -components are unequally spaced, in contrast to the unperturbed pattern.

Figure 1 indicates the positions of perturbed and unperturbed components in an imaginary example.

The wave numbers in table 2 are experimental values that give the adopted values for the displaced levels from which the wave numbers of the components have been recalculated. The decimal parts of the resulting values are listed in table 2 under the corresponding observed value for comparison. The close agreement between calculated and observed values in table 2 proves the validity of the combination principle when applied to an asymmetrical pattern and hence the possibility of computing values for the displaced levels with the observed wave numbers.

The observed intervals between the consecutive magnetic levels are thus unequal, being 7.09, 7.39, and 7.67 for a $^6D_{1\frac{1}{2}}$, and 6.43, 6.50, 6.54, 6.62, and 6.67 for z $^6D_{2\frac{1}{2}}^{\circ}$. The differences, in both cases, cannot be ascribed to experimental errors but are clearly due to an asymmetry.

At the bottom of table 2 the pattern for another line $a {}^{6}D_{114} - z {}^{6}D_{014}$ is included. This Mn I line has the level $a {}^{6}D_{114}$ in common with the other. From

the observed components one may calculate the perturbed magnetic levels as before. The resulting values for the magnetic levels belonging to $a^6 D_{1\%}$ are exactly the same as those for the line 24485.25 and hence show the same perturbed intervals 7.09, 7.39, 7.67. Many other examples could be presented to prove the existence of asymmetrical patterns. All of them show the same singularities. The irregularities in the displacements are exactly the same for all lines having their origins in the level involved.

3. Asymmetrical Pattern in Theory

In 1913, while observing the Zeeman effect of the line 6708 A of lithium, Paschen and Back found that the observed pattern was in complete contradiction with the Preston rule. It is a close doublet, and there is a sort of interaction between the effects of the two lines forming it. Similar results were obtained for other close doublets and triplets, although lines that are not organically connected do not show this effect, even though their wavelengths may be very close to each other. This interaction was called the Paschen-Back effect. In some cases the observed Zeeman patterns for very close multiplets exhibit a sort of distortion due to partial Paschen-Back effect, the field in these cases not being strong enough for a complete interaction but only sufficient to alter the normal pattern.

The theory of the Paschen-Back effect has been developed in detail by different authors. Kiess and Shortley [7] have recently considered the distorted patterns in the oxygen and nitrogen spectra, and have found a quantitative theoretical explanation of them. The multiplets $3s^3S^{\circ}-3p^3P$ and $3s^5S^{\circ}-3p^5P$ of O1 at 8446 and 7771 A with the narrow intervals 0.5, 0.7 and 2.0, 3.7 cm⁻¹ show a great distortion.

Table 2. Observed perturbed patterns for lines 24485.25 and 24630.08 of Mn I [LU=3.955 cm⁻¹; levels 42053.73, 42198.56, and 17568.48]

				7	a 6 D 1 1/4			
M	Level	$M = -1\frac{1}{2}$	ź - l	M=-0	0½	$M=0^{1/2}$	í	$M=1\frac{1}{2}$
		17557.53	7.09	17564.62	7.39	17572.01	7.67	17579.68
$-2\frac{1}{2}$	42037.41	24479.88 .88		,				
	6.43	.00						
$-1\frac{1}{2}$	42043.84	24486.32	7.11	24479. 21 .22				
	6.50	.01					01335	
$-0\frac{1}{2}$	42050.34	24492.84	7.12	24485.72 .72	7.40	24478.32 .33		
z $^6\mathrm{D}^\circ_{2\frac{1}{2}}$	6.54	,02						
$0\frac{1}{2}$	42056.88			24492.23 .26	7.35	24484.88 .87	7.70	24477.18 .20
	6.62							
$1\frac{1}{2}$	42063.50					24491.49 .49	7.66	24483.83
	6.67							
$2\frac{1}{2}$	42070.17							24490.49 .49
$-0\frac{1}{2}$	42192.45	24634.93 .92	7.09	24627.84 .83	7.42	24620.42 .44		
z 6D°	13.10	.02						
$0\frac{1}{2}$	42205.55			24640.91 .93	7.37	24633.54 .54	7.67	24625.87 .87

The multiplet of N I, 3s ⁴P-3p ⁴S° at 7423 to 7468 A, with greater intervals, namely 46.7, 33.8, shows much smaller distortion. The results of Kiess and Shortley for N I, in a multiplet with the relatively wide separations, 46.7 and 33.8, indicate clearly that multiplets with relatively great intervals, in other elements, could be expected to show also measurable Paschen-Back interaction. This conclusion suggested to the writer the likelihood that the observed distortions in Mn I are due to a similar effect. In order to prove this hypothesis the structure of the levels so affected was considered in some detail.

According to the second order perturbation theory [7, p. 204] magnetic levels having the same magnetic numbers M, and belonging to spectroscopic levels which differ by one unit in J-value, and to the same term, repel each other by an amount, ϵ , equal to

$$\epsilon = \frac{I^2}{\delta},$$
 (1)

all quantities being expressed in Lorentz units. In this formula δ is the distance between the two magnetic levels under consideration. Within the accuracy of eq 1 δ represents either the perturbed or the unperturbed distance. The factor I is the interaction element; its values depend only on the particular values of S, L, J, and M for the levels involved. Equation 2 gives the dependence of I on the quantum numbers in Lorentz units, LU:

$$\sqrt{\frac{(J-L+S)(J+L-S)(L+S+1+J)(L+S+1-J)}{4J^{2}(2J-1)(2J+1)}}\sqrt{J^{2}-M^{2}}. \tag{2}$$

Here the value J is the larger of the two J-values involved. The energy perturbation is to be applied to each of the states always in the repulsive direction. If more than two states interact, the perturbations of each pair may be supposed to operate independently.

The writer has computed with formula (2) the values of I^2 and I for the different cases. The resulting values are given in table 3 with the I-values above and the I^2 -values below. In general the values of the interaction element increase when either S or L increases and decrease when either J or M increases. Hence the greatest interactions are expected in terms of high multiplicities and high L-values, and, within a term, the greatest interactions may be expected in the levels with smaller J- and M-values. A very important conclusion is that the sign of M does not affect the I-values because M appears in eq 2 as a square. The same I factor corresponds to level (+M) as to (-M)

Because the measured distances between magnetic components and, therefore, the level-separations are expressed in wave numbers, cm⁻¹, it is desirable to express the values of I in the same units. This is done by multiplication by the Lorentz unit (LU), which is $a=4.669\times10^{-5}\,H\,\mathrm{cm}^{-1}$,

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Table 3. Values for the interaction element, I, and its squares [Upper figures are I-values in Lorentz units; lower I²-values, in $(LU)^2$]

Even	multiplicities		No.			
Interaction between—				$M(\pm)$		
	0.	1/2	1½	21/2	31/2	41/2
² P _{1½} and ² P _{0½}		471 222				
$^2\mathrm{D}_{21/4}$ and $^2\mathrm{D}_{11/4$		490 240	0. 400 0. 160		/	
² F _{3½} and ² F _{2½}		495 245	0. 452 0. 204	0. 350 0. 122		
4P _{1½} and 4P _{0½}		745 556				
$^4P_{2\frac{1}{2}}$ and $^4P_{1\frac{1}{2}}$		600 360	0. 490 0. 240			
⁴ D _{1½} and ⁴ D _{0½}	(1.)	000				
$^4\mathrm{D}_{2\%}$ and $^4\mathrm{D}_{1\%}$	(0, 8	916 840	0. 748 0. 560			
⁴ D _{3½} and ⁴ D _{2½}	0. 4	700 490	0. 639 0. 408	0. 495 0. 245		
⁴ F _{2½} and ⁴ F _{1½}	(0. 8		0. 800 0. 640			
⁴ F _{3½} and ⁴ F _{2½}	$\begin{bmatrix} 0.9 \\ 0.9 \end{bmatrix}$		0. 875 0. 765	0. 678 0. 459		
⁴ F _{41/4} and ⁴ F _{31/4}	$ \left\{ \begin{array}{c} 0.7 \\ 0.5 \end{array} \right. $		0. 707 0. 500	0. 624 0. 389	0. 471 0. 222	
⁴ G ₃₁₄ and ⁴ G ₂₁₄	0. 9 0. 9		0. 875 0. 765	0. 678 0. 459		
⁴ G ₄₁₄ and ⁴ G ₃₁₄	$\begin{cases} 0.9 \\ 0.9 \end{cases}$		0. 925 0. 856	0. 816 0. 665	0. 617 0. 380	
⁴ G _{51/4} and ⁴ G _{41/2}	$\begin{cases} 0.7 \\ 0.5 \end{cases}$		0. 745 0. 555	0. 690 0. 476	0. 598 0. 357	0. 445 0. 198
$^6\mathrm{P}_{2\!/\!_4}$ and $^6\mathrm{P}_{1\!/\!_2}$	$$ $\left\{ \begin{array}{c} 0.7 \\ 0.5 \end{array} \right.$	60	0. 611 0. 373			
$^6\mathrm{P}_{31/4}$ and $^6\mathrm{P}_{21/4}$	$\left\{\begin{array}{c} 0.6 \\ 0.4 \end{array}\right.$		0. 583 0. 340	0. 452 0. 204		
⁶ D _{1½} and ⁶ D _{0½-}	$$ $\left\{ \begin{array}{c} 1.2 \\ 1.5 \end{array} \right.$	47 56				1
$^6\mathrm{D}_{214}$ and $^6\mathrm{D}_{114}$	\begin{cases} 1. 20 \\ 1. 44 \end{cases}		0. 980 0. 960			
$^3\mathrm{D}_{31/2}$ and $^6\mathrm{D}_{21/2}$	$\begin{bmatrix} 1.08 \\ 1.10 \end{bmatrix}$		0. 958 0. 918	0. 742 0. 551		
$^6\mathrm{D}_{41/2}$ and $^6\mathrm{D}_{31/2}$	$ \begin{cases} 0.78 \\ 0.61 \end{cases} $		0. 745 0. 556	0. 657 0. 432	0. 497 0. 247	
F _{11/4} and ⁶ F _{01/4}	$\left\{\begin{array}{c} 1.49 \\ 2.22 \end{array}\right.$					
F _{2½} and ⁶ F _{1½}	$$ $\left\{ \begin{array}{c} 1.47 \\ 2.16 \end{array} \right.$		1. 200 1. 440			
F_{314} and ${}^{6}F_{234}$	$\left\{\begin{array}{c} 1.35 \\ 1.83 \end{array}\right.$		1. 237 1. 531	0. 958 0. 918		

Table 3. Values for the interaction element, I, and its squares—Continued [Upper figures are I-values in Lorentz units; lower I^2 -values, in $(LU)^2$]

	Even multip	licities				
				$M(\pm)$		
Interaction between—		0½	1½	2½	3½	41/2
$^6\mathrm{F}_{41\!/_2}$ and $^6\mathrm{F}_{31\!/_2$		$ \left\{ \begin{array}{c} 1.165 \\ 1.358 \end{array} \right. $	1. 086 1. 179	0. 975 0. 951	0. 737 0. 543	
$\mathrm{F}_{51\!/\!_{2}}$ and $\mathrm{^6F}_{41\!/\!_{2}}$		$\left\{\begin{array}{c} 0.862 \\ 0.744 \end{array}\right.$	0. 833 0. 694	0. 771 0. 595	0. 668 0. 446	0. 498 0. 248
$\mathrm{G}_{2lambda_{5}}$ and ${}^{6}\mathrm{G}_{1lambda_{5}}$		$\left\{\begin{array}{c} 1.414 \\ 2.000 \end{array}\right.$	1. 155 1. 333			
$^{6}\mathrm{G}_{352}$ and $^{6}\mathrm{G}_{252}$		$ \left\{ \begin{array}{c} 1.498 \\ 2.245 \end{array} \right. $	1, 368 1, 871	1. 059 1. 122		
$^6\mathrm{G}_{4\slash\hspace{-0.07cm}4}$ and $^6\mathrm{G}_{3\slash\hspace{-0.07cm}4}$		$\left\{\begin{array}{c} 1.414 \\ 2.000 \end{array}\right.$	1. 342 1. 800	1. 183 1. 400	0. 894 0. 800	
$^6\mathrm{G}_{51\!/\!_2}$ and $^6\mathrm{G}_{41\!/\!_2}$		$\left\{\begin{array}{c} 1.226 \\ 1.504 \end{array}\right.$	1. 185 1. 404	1. 097 1. 203	0. 950 0. 903	0. 708 0. 501
$^6\mathrm{G}_{6\!\!\times\!\!4}$ and $^6\mathrm{G}_{5\!\!\times\!\!4}$		\[\begin{pmatrix} 0.910 \\ 0.828 \end{pmatrix} \]	0. 888 0. 789	0. 843 0. 710	0. 769 0. 592	0. 659 0. 434
	Odd multip	olicities				
Interaction between—			M(土)		
Interaction between-	0	1	2	3	4	5
³ P ₁ and ³ P ₀	$\left\{\begin{array}{c} 0.817 \\ 0.667 \end{array}\right.$					
$^3\mathrm{P}_2$ and $^3\mathrm{P}_{1-}$	$\left\{\begin{array}{c} 0.577 \\ 0.333 \end{array}\right.$	0. 500 0. 250				
$^3\mathrm{D}_2$ and $^3\mathrm{D}_{1$	$\left\{\begin{array}{c} 0.775 \\ 0.600 \end{array}\right.$	0. 671 0. 450				
$^3\mathrm{D}_3$ and $^3\mathrm{D}_2$	$\left\{\begin{array}{c} 0.632 \\ 0.400 \end{array}\right.$	0. 596 0. 356	0. 471 0. 222			
$^3\mathrm{F}_3$ and $^3\mathrm{F}_2$	$\left\{\begin{array}{c} 0.756 \\ 0.571 \end{array}\right.$	0. 713 0. 508	0. 563 0. 318			
³ F ₄ and ³ F ₃	$ \left\{ \begin{array}{c} 0.655 \\ 0.429 \end{array} \right. $	0. 634 0. 402	0. 567 0. 321	0. 433 0. 188		
$^3\mathrm{G}_4$ and $^3\mathrm{G}_{3$	$\left\{\begin{array}{c} 0.745 \\ 0.556 \end{array}\right.$	0. 722 0. 521	0. 646 0. 417	0. 493 0. 243		
$^3\mathrm{G}_5$ and $^3\mathrm{G}_{4$	$\left\{ \begin{array}{c} 0.667 \\ 0.444 \end{array} \right.$	0. 653 0. 428	0. 611 0. 373	0. 533 0. 284	0. 400 0. 160	
$^5\mathrm{P}_2$ and $^5\mathrm{P}_1$	$\left\{\begin{array}{c} 0.775 \\ 0.600 \end{array}\right.$	0. 671 0. 450				
$^5\mathrm{P}_3$ and $^5\mathrm{P}_2$	$\left\{\begin{array}{c} 0.632 \\ 0.400 \end{array}\right.$	0. 596 0. 356	0. 471 0. 222			
$^5\mathrm{D}_1$ and $^5\mathrm{D}_0$	$\left\{\begin{array}{c} 1.414 \\ 2.000 \end{array}\right.$					
$^5\mathrm{D}_2$ and $^5\mathrm{D}_1$	$- \left\{ \begin{array}{c} 1, 183 \\ 1, 400 \end{array} \right.$	1. 025 1. 050				
$^5\mathrm{D}_3$ and $^5\mathrm{D}_2$	$-\left\{\begin{array}{c} 1.014 \\ 1.029 \end{array}\right.$	0. 956 0. 914	0. 756 0. 571			
⁵ D ₄ and ⁵ D ₃	$ \begin{cases} 0.756 \\ 0.571 \end{cases} $	0. 732 0. 536	0. 655 0. 429	0. 500 0. 250		

Table 3. Values for the interaction element, I, and its squares—Continued [Upper figures are I-values in Lorentz units; lower I²-values, in $(LU)^2$]

	Odd multip	onercies				
Interaction between—			M((±)		
	0	1	2	3	4	5
$^5\mathrm{F}_2$ and $^5\mathrm{F}_1$	1. 265 1. 600	1. 095 1. 200				
$^5\mathrm{F}_3$ and $^5\mathrm{F}_2$	$ \left\{ \begin{array}{c} 1.242 \\ 1.543 \end{array} \right. $	1. 171 1. 371	0. 926 0. 857			
⁵ F ₄ and ⁵ F ₃	1. 091 1. 190	1. 056 1. 116	0. 945 0. 893	0. 722 0. 521		
$^5\mathrm{F}_5$ and $^5\mathrm{F}_4$	0. 816 0. 667	0. 805 0. 640	0. 748 0. 560	0. 653 0. 427	0. 490 0. 240	
$^5\mathrm{G}_3$ and $^5\mathrm{G}_{2$	$ \begin{cases} 1, 195 \\ 1, 429 \end{cases} $	1. 127 1. 270	0. 891 0. 794			
⁵ G ₄ and ⁵ G ₃	$ \begin{cases} 1, 254 \\ 1, 571 \end{cases} $	1. 214 1. 473	1. 086 1. 179	0. 829 0. 688		
$^5\mathrm{G}_5$ and $^5\mathrm{G}_{4$	$ \begin{cases} 1.101 \\ 1.273 \end{cases} $	1. 105 1. 222	1. 034 1. 069	0. 903 0. 815	0. 677 0. 458	
$^5\mathrm{G}_6$ and $^5\mathrm{G}_5$	$ \begin{cases} 0.853 \\ 0.727 \end{cases} $	0. 841 0. 707	0. 804 0. 647	0. 739 0. 546	0. 636 0. 404	0. 47 0. 22
⁷ P ₃ and ⁷ P ₂	$ \begin{cases} 0.756 \\ 0.571 \end{cases} $	0. 713 0. 508	0. 563 0. 318			
⁷ P ₄ and ⁷ P ₃	$ \begin{cases} 0.655 \\ 0.429 \end{cases} $	0. 634 0. 402	0. 567 0. 321	0. 433 0. 188		
$^7\mathrm{D}_2$ and $^7\mathrm{D}_1$	$ \begin{cases} 1, 265 \\ 1, 600 \end{cases} $	1. 095 1. 200				
$^7\mathrm{D}_3$ and $^7\mathrm{D}_2$	$ \begin{cases} 1, 242 \\ 1, 543 \end{cases} $	1. 171 1. 371	0. 926 0. 857			
⁷ D ₄ and ⁷ D ₃	\bigg\{ \bigcup_{1, 191} \\ 1, 191 \end{array}	1. 056 1. 116	0. 945 0. 893	0. 722 0. 521		
$^7\mathrm{D}_5$ and $^7\mathrm{D}_{4$	0. 816 0. 667	0. 800 0. 640	0. 748 0. 560	0. 653 0. 427	0. 490 0. 240	
$^7\mathrm{F}_1$ and $^7\mathrm{F}_0$	$\left\{\begin{array}{c} 2.000 \\ 4.000 \end{array}\right.$					
$^7\mathrm{F}_2$ and $^7\mathrm{F}_1$	$ \begin{cases} 1.732 \\ 3.000 \end{cases} $	1. 500 2. 250				
$^7\mathrm{F}_3$ and $^7\mathrm{F}_2$	$\left\{\begin{array}{c} 1.604 \\ 2.573 \end{array}\right.$	1. 512 2. 286	1. 195 1. 429			
$^7\mathrm{F}_4$ and $^7\mathrm{F}_3$	$ \begin{cases} 1.447 \\ 2.095 \end{cases} $	1. 402 1. 964	1. 254 1. 571	0. 957 0. 917		
⁷ F ₅ and ⁷ F ₄	$\left\{\begin{array}{c} 1.231 \\ 1.515 \end{array}\right.$	1. 206 1. 455	1. 128 1. 273	0. 985 0. 970	0. 739 0. 546	
$^7\mathrm{F}_6$ and $^7\mathrm{F}_5$	$ \begin{cases} 0.905 \\ 0.818 \end{cases} $	0. 892 0. 796	0. 853 0. 727	0. 783 0. 614	0. 674 0. 455	0. 50 0. 25

H being the field strength in oersteds.

If the repulsion in this case is e, and the separation is Δ , eq 1 can be written

$$e = \frac{I^2}{\Delta} a^2 \text{ cm}^{-1}, \tag{3}$$

where

$$a^2 = (4.669 \times 10^{-5} H)^2 = 21.80 \times 10^{-10} H^2 \text{ cm}^{-2}$$
. (4)

Since I^2 is a function of M^2 , in the following the factor I^2/Δ will be set as $f(M_J^2)$. In this notation

eq 3 will be

$$e = a^2 f(M_J^2). (5)$$

The values of function f being the same for (+M)as for (-M), we can write

$$f(M_J^2) = f[(-M)_J^2].$$
 (6)

Before we preceed to the computation of the effects for some Mn I lines it is of interest to estimate roughly the intervals between levels necessary to obtain measurable distortions, with a magnetic field of about 80,000 oersteds, which is close to the fields used for our spectrograms.

From eq 3 and 4 we can write

$$\Delta = \frac{I^2}{e} a^2 = \frac{I^2}{e} 21.80 \times 10^{-10} \times 80,000^2 = \frac{I^2}{e} \times 17 \text{ cm}^{-1}.$$
(7)

The accuracy of the measured wave numbers evidently depends on the region of the spectrum. At about 25,000 cm⁻¹ (4,000 Å) the accuracy, in the MIT spectrograms, is close to 0.05 cm⁻¹. This is the minimum value that e can have if measurable effects are to be observed. We can then write

$$\Delta = \frac{17}{0.05} I^2 \simeq 340 I^2 \,\mathrm{cm}^{-1}. \tag{8}$$

Equation 8 is a relation between the interval Δ and the interaction factor. If we select a transition for which I^2 is approximately one unit (see table 3), observable effects will be possible with intervals Δ smaller than 340 cm⁻¹. In cases in which the I^2 -values are greater than one unit, such as those in the $^6\mathrm{D}$ and $^6\mathrm{F}$ terms, much wider intervals will still show asymmetries. Because the term intervals in Mn I rarely exceed 200 cm⁻¹, it is possible to find many asymmetries in it.

The foregoing estimate shows clearly why so many asymmetries have been noted in the past by observers of the Zeeman effect. The asymmetrical patterns belong not only to the spectra of the light elements that have narrow term intervals, but also to elements of high atomic numbers whose term intervals are much wider. In these cases the I^2 -values are sufficiently great for the intervals to

show measurable asymmetries.

4. Positions of Magnetic Levels Affected by Partial Paschen-Back Effect

A spectroscopic level T_J , by influence of the magnetic field, is split up into 2J+1 magnetic levels T_J^{M} , whose values are given by

$$T_J^M = T_J + M_J a q_J$$
.

We shall consider first the simplest case in which only one other level, T_{J-1} , exists close to the level T_J of the same term. Suppose that the relative value of T_J is smaller than that of T_{J-1} . The magnetic levels of T_J will be lowered in value by the repulsions due to the magnetic levels of T_{J-1} . The amounts of these displacements are given by eq 5 so that the final values of these perturbed magnetic levels T'_J^M will be

$$T_J^{\prime M} = T_J + M_J a g_J - a^2 f(M_J^2).$$
 (9)

The whole set of magnetic levels of T_J is lowered in value because the repulsions are all in the same direction; the magnitudes of these displacements are different for the individual levels on account of the different values that the function $f(M_J^2)$ has for different M_J -values. Figure 2 illustrates the relative positions of the perturbed magnetic levels of T_J , compared with the unperturbed positions.

Levels with the same M-value have the same displacement independent of the sign of M; thus, all levels $M = \pm 0$ % have experienced a displacement a, and all with $M=\pm 1$ ½ have been displaced by an amount b. The direction of the displacements in $T_{2\frac{1}{2}}$ is contrary to that in $T_{1\frac{1}{2}}$. Levels $\dot{M}=\pm 2\frac{1}{2}$ have not experienced displacement because there are no magnetic levels with such M-values in the level $T_{1\frac{1}{2}}$.

The intervals between consecutive magnetic levels, such as those having magnetic quantum values M_J and M_J-1 , may be computed by eq 9. The resulting value is

$$\Delta T'_{J,J}^{M,M-1} = [M_J - (M_J - 1)] a g_J - a^2 f(M_J^2) + a^2 f[(M_J - 1)^2],$$

$$\Delta T_{J,J}^{M,M-1} = a g_J - a^2 f(M_J^2) + a^2 f[(M_J - 1)^2].$$
 (10)

The intervals are unequal because of the influence of the quadratic terms, which have different values for the different M-values. Figure 2 shows clearly this inequality. The pertrubed magnetic levels appear to approach each other in the opposite direction of the perturbing level.

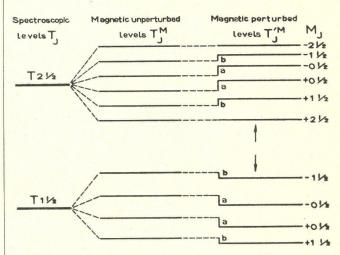


Figure 2. Mutual repulsions between the magnetic levels of $T_{2\frac{1}{2}}$ and $T_{1\frac{1}{2}}$

The magnetic levels with the same M-value repel each other. The magnitude of the displacements a or b, due to the repulsion, depends on the absolute value of M, but is independent of the sign of M.

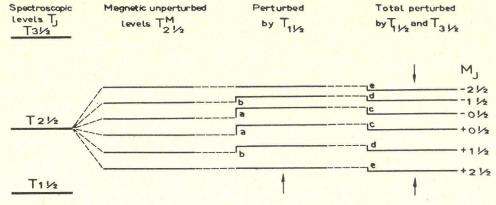


Figure 3. Perturbation of magnetic levels of $T_{25/2}$ due to the proximity of the magnetic levels of $T_{15/2}$ and $T_{25/2}$.

The perturbations that arise from T_{134} and T_{334} may be considered to act independently. By influence of the magnetic levels of T_{134} those of T_{234} are displaced upward by amounts a or b. These partially perturbed levels are displaced downward by amounts c, d, or e, by influence of magnetic levels of T_{334} .

The separations between two magnetic levels having the same M-value but different sign are

$$\Delta T'_{J,-J}^{+M,-M} = M_J a g_J - (-M)_J a g_J - a^2 f(M_J^2) + a^2 f[(-M)_J^2].$$

But the quadratic terms being equal by eq 6 cancel, and thus we have

$$\Delta T^{\prime + M, -M} = 2M_J a g_J. \tag{11}$$

This final equation is independent of quadratic terms, and hence we conclude that the separation between the perturbed levels is, in this particular case, independent of the perturbation and thus equal to the separation between unperturbed levels. Hence we can write

$$\Delta T^{\prime + M, -M} = \Delta T_{J, J}^{+M, -M}. \tag{12}$$

We are now prepared to discuss the general case in which the affected level is perturbed simultaneously by two levels of the same term, one on each side of it. Figure 3 gives an illustration of this case. The level $T_{2\frac{1}{2}}$ is perturbed by the two close levels $T_{3\frac{1}{2}}$ and $T_{1\frac{1}{2}}$. In order to obtain the final perturbed levels, it is

In order to obtain the final perturbed levels, it is necessary to consider independently the influences of T_{J-1} and T_{J+1} . Each of these influences will give a quadratic term to the equation, but as they are situated on opposite sides of T_J , the signs will be different for the two quadratic terms. By the simple case explained before we know that the displacements are always in a contrary sense to the perturbing level. The final values of the magnetic levels will then be

$$T_J^{\prime M} = T_J + M_J a q_J - a^2 f(M_J^2) + a^2 f(M_{J+1}^2),$$
 (13)

 $a^2 f(M_J^2)$ being the perturbation due to T_{J-1} and $a^2 f(M_{J+1}^2)$ that due to the level T_{J+1} .

The intervals between two consecutive levels with quantum numbers M_J and M_J-1 by eq 13 are

$$\Delta T'_{JJ}^{\mu,M-1} = a g_J - a^2 f(M_J^2) + a^2 f(M_{J+1}^2) + a^2 f[(M_J - 1)^2] - a^2 f[(M_{J+1} - 1)^2], \quad (14)$$

or

$$\Delta T_{JJ}^{M,M-1} = a g_J + \text{four quadratic terms.}$$

The separations between levels with the same absolute value of M, but contrary sign, are

$$\begin{split} \Delta T'^{-M}_{J,} + ^{+M}_{J} = & M_{J} a \, g_{J} - (-M)_{J} \, a \, g_{J} - a^{2} f(M_{J}^{2}) + \\ & a^{2} f(M_{J+1}^{2}) + a^{2} f[(-M)_{J}^{2}] - a^{2} f[(-M)_{J+1}^{2}], \end{split}$$

but this equation by eq 6 will be

$$\Delta T'^{-M} = 2 M_J a q_J, \tag{15}$$

a result that shows that the separations are independent of the quadratic terms and therefore equal to those of the unperturbed levels.

The magnitude of the displacements given by (3) decreases when the J-values increase owing to the influence of I and Δ . Table 3 shows that in a term I decreases as J increases. In spectral terms that follow Landé's interval rule, Δ increases with J; the function given by eq 5 will hence decrease when J increases. In general this means that in a level T_J the perturbations due to T_{J-1} are expected to be greater than those due to T_{J+1} , and hence after the final perturbation the levels will appear close to each other in the direction of T_{J+1} as shown in figure 3.

5. Positions of Components in an Asymmetric Pattern

The wave numbers of perturbed lines formed by transitions between perturbed magnetic levels T'_{J} and $U^{\circ'}_{J'}$ are evidently given by

$$n'_{I'}^{M,M'} = T'_{I'}^{M} - U^{\circ'M'}_{I'},$$

but introducing here the level values given by eq 9,

Table 5. Magnetic levels and g-values in IMn [magnetic field 84,700 oersteds; LU=3.955 cm-1]

Spectroscopic levels,	Magnetic quantum	Diants				Mag	gnetic levels			
T_{J}	$\frac{\text{quantum}}{\text{number}}$	Displacements M _J ag _J	Pertu	rbations	Total dis- placements	T_J^M Unperturbed	T' M Pe	rturbed	Interval, observed	g-values ob- served
	$(-2\frac{1}{2})$	-16. 38	0.05				Calculated	Observed		1
$a^{6}\mathrm{D}_{256} \ 17451.52 \ g_{256} = 1.657$	$ \begin{cases} -2/2 \\ -1/2 \\ -0/2 \\ 0/2 \\ 1/2 \\ 21/2 \end{cases} $	-16. 38 -9. 83 -3. 28 3. 28 9. 83 16. 38	0. 05 0. 09 0. 10 0. 10 0. 09 0. 05	-0. 13 -0. 19 -0. 19 -0. 13	$ \begin{array}{r} -16.33 \\ -9.89 \\ -3.37 \\ 3.19 \\ 9.77 \\ 16.43 \end{array} $	17435. 14 17441. 69 17448. 24 17454. 80 17461. 35 17467. 90	. 19 . 63 . 15 . 71 . 29 . 95	. 18 . 65 . 15 . 71 . 30 . 97	6. 47 6. 50 6. 56 6. 59 6. 67	1. 658 1. 657 1. 659
$a ^6\mathrm{D}_{154} \ 17568. 48 \ g_{154} \! = \! 1. 867$	$ \begin{cases} -1\frac{1}{2} \\ -0\frac{1}{2} \\ 0\frac{1}{2} \\ 1\frac{1}{2} \end{cases} $	-11. 08 -3. 69 3. 69 11. 08	0. 13 0. 19 0. 19 0. 13	$ \begin{array}{c} -0.35 \\ -0.35 \\ -0.35 \end{array} $	$ \begin{array}{r} -10.95 \\ -3.85 \\ 3.53 \\ 11.21 \end{array} $	17557. 40 17564. 79 17572. 17 17879. 56	. 53 . 63 . 01 . 69	. 53 . 62 . 01 . 68	7. 09 7. 39 7. 67	1. 867 1. 868
$a^{6}\mathrm{D}_{014} \ 17637.\ 15 \ g_{014} = 3.\ 333$	$\begin{cases} -0\frac{1}{2} \\ 0\frac{1}{2} \end{cases}$	-6. 59 6. 59	0. 35 0. 35		$\begin{bmatrix} -6.24 \\ 6.94 \end{bmatrix}$	17630. 56 17643. 74	. 91 4. 09	. 94 4. 11	13. 17	3. 330
z $^{6}\mathrm{D}_{256}^{2}$ 42053. $73g_{256}^{2} = 1. 657$	$\begin{cases} -2\frac{1}{2} \\ -1\frac{1}{2} \\ -0\frac{1}{2} \\ 0\frac{1}{2} \\ 0\frac{1}{2} \\ 1\frac{1}{2} \\ 2\frac{1}{2} \end{cases}$	$\begin{array}{c} -16.38 \\ -9.83 \\ -3.28 \\ 3.28 \\ 9.83 \\ 16.38 \end{array}$	0. 07 0. 12 0. 14 0. 14 0. 12 0. 07	$ \begin{array}{c} -0.17 \\ -0.25 \\ -0.25 \\ -0.17 \end{array} $	$ \begin{array}{r} -16.31 \\ -9.88 \\ -3.39 \\ 3.39 \\ 9.78 \\ 16.45 \end{array} $	42037. 35 42043. 90 42050. 45 42057. 01 42063. 56 42070. 11	. 42 . 85 . 34 6. 90 . 51	. 41 . 84 . 34 6. 88 . 50 . 17	6. 43 6. 50 6. 54 6. 62 6. 67	1. 657 1. 657 1. 654
$z^{6}\mathrm{D}_{114}^{\circ} \ 42143.57 \ g_{114}\!=\!1.867$	$ \begin{cases} -\frac{1\frac{1}{2}}{-0\frac{1}{2}} \\ -\frac{0\frac{1}{2}}{0\frac{1}{2}} \\ \frac{0\frac{1}{2}}{1\frac{1}{2}} \end{cases} $	$ \begin{array}{c c} -11.08 \\ -3.69 \\ 3.69 \\ 11.08 \end{array} $	0. 17 0. 25 0. 25 0. 17	-0. 44 -0. 44	$ \begin{array}{r} -10.91 \\ -3.88 \\ 3.50 \\ 11.25 \end{array} $	42132. 49 42139. 89 42147. 26 42154. 65	. 66 . 69 . 07 . 82	. 67 . 70 . 09 . 79	7. 03 7. 39 7. 70	1. 864 1. 868
$z^{6}\mathrm{D}_{0\%}^{8}$ 42198. 56 $g_{0\%}\!=\!3.333$	$ \begin{bmatrix} -0\frac{1}{2} \\ 0\frac{1}{2} \end{bmatrix} $	-6. 59 6. 59	0. 44 0. 44		-6. 15 7. 03	42191, 97 42205, 15	2. 41 . 59	2. 45 . 55	13. 10	3. 312
$z^{6} F_{234}^{2} 43595.50 g_{234} = 1.314$	$ \begin{pmatrix} -2\frac{1}{2} \\ -1\frac{1}{2} \\ -0\frac{1}{2} \\ 0\frac{1}{2} \\ 1\frac{1}{2} \\ 2\frac{1}{2} \end{pmatrix} $	$ \begin{array}{c} -12.99 \\ -7.80 \\ -2.60 \\ 2.60 \\ 7.80 \\ 12.99 \end{array} $	0. 20 0. 34 0. 40 0. 40 0. 34 0. 20	-0. 46 -0. 69 -0. 69 -0. 46	$ \begin{array}{r} -12.79 \\ -7.92 \\ -2.89 \\ 2.31 \\ 7.68 \\ 13.19 \end{array} $	43582, 51 43587, 70 43592, 90 43598, 10 43603, 30 43608, 49	. 71 . 58 . 61 7. 81 . 18 . 69	. 71 . 56 . 61 7. 79 . 14 . 65	4. 85 5. 05 5. 18 5. 35 5. 51	1. 313 1. 313 1. 310
z^{6} F _{1½} 43644. 45 $g_{1½}$ =1. 067	$\begin{cases} -\frac{1}{2} \\ -\frac{0}{2} \\ 0\frac{1}{2} \\ \frac{1}{2} \end{cases}$	$ \begin{array}{c} -6.33 \\ -2.11 \\ 2.11 \\ 6.33 \end{array} $	0. 46 0. 69 0. 69 0. 46	$ \begin{array}{c c} -1.22 \\ -1.22 \\ -1.22 \end{array} $	-5. 87 -2. 64 1. 58 6. 79	43638. 12 43642. 34 43646. 56 43650. 78	. 58 1. 81 6. 03 1. 24	. 59 1. 97 5. 95 1. 25	3. 38 3. 98 5. 30	1. 067 1. 006
$z {}^{6}F_{01/2}^{8}$ 43672.96 $g_{01/2} = 0.667$	$\begin{bmatrix} -0\frac{1}{2} \\ 0\frac{1}{2} \end{bmatrix}$	1. 32 -1. 32	1. 22 1. 22		2. 54 -0. 10	43674. 28 43671. 64	5. 50 2. 86	5. 32 2. 94	-2.38	$-\bar{0}.\bar{6}\bar{0}\bar{2}$

ments. Lines marked with an asterisk (*) indicate poor measurements because of the close proximity of another line.

With the observed wave numbers a system of observed levels was derived. The values of the observed magnetic levels are listed under their respective theoretical values in table 6. To check the accuracy of the measurements, these observed values have been used to recalculate the wave numbers. The resulting values (only the decimal parts) are given between calculated and observed values in table 6. With very few exceptions the values agree to 1 or 2 units in the last decimal, thus indicating that the measurements are very consistent. The close agreement between the ob-

served wave numbers and those derived for the observed magnetic levels is strong proof that the combination principle applies exactly to asymmetric patterns.

The observed magnetic levels thus computed have also been listed for comparison purposes in table 5, where for simplicity, only the decimal parts of their values are given in column 9. The observed intervals between consecutive levels, listed in column 10, are evidently unequal, as expected from theory. If the calculated and observed values for the perturbed levels given in table 5 are compared with each other, it will be observed that in most cases the agreement is extremely good—rarely exceeding the differences by more than 0.02 cm⁻¹—in spite of the

Table 6. Asymmetric Zeeman patterns in multiplets a *D-z *Do and a *D-z *Fo of Mn I (field 84,700 oersteds)

a ⁶ D _o _½ =17637.15		15.77							75 77	78 24495. 60 76 . 59 75	6 24502. 98 .5 . 98 .5 3. 00	24510. 73	50 24548. 32 51 . 34 43* . 33	8 24561, 50
a &De	-01/2	17630. 91				1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	24501.7	24508.7	24516. 16 . 15		24561.	24574. 68
	11/2	.67 17559.69 .68				24477. 21 . 20 . 18	24483. 82 . 82 . 83	24490. 49 . 49			24567. 38	24575.13		24625.90
a ⁶ D ₁₅ =17568.48	\$40	38 17572.01 .01			24478. 33 33	24484. 89 . 87 . 88	24491. 50 . 49 . 49			24567. 68	24675.06	24582. 81	24620. 40	24633, 58
a 6D11/2=	-01/2	.09 17564. 63 . 62		24479. 23 . 22 . 21	24485. 71 . 72 . 72	24492. 27 . 26 . 23			24568. 03	24575. 06	24582. 44		24627. 78 . 83 . 84	24640.96
	-11/2	7. 17557. 53 . 53	24479. 89 . 88 . 88	24486. 32 . 31 . 32	24492. 81 . 81				24575. 13	24582. 16			24634. 88 . 92 . 93	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
	21/2	.67 17467.95 .97					24595. 56	24602. 23 . 20		1 J I 1		24686. 87 . 82 . 84		
	11/2	.59 6 17461. 29 .30				24595. 61	24602. 22	24608. 89 . 87			24685. 78 . 79 . 79	24693. 53 . 49 . 50		
	01/2	655 6 17454. 71 . 71			24595. 63	24602. 19	24608. 80			2468. 98 . 99 5. 02	24692. 36 . 38 . 39	24700. 11 . 08 . 06		
a 6D ₂ ½=17451.52	-01/2	6. 17448. 15 . 15		24595. 70	24602. 19	24608. 75		. 1 1	24684. 51 . 52 . 54	24691. 54 . 55 . 55	24698. 92 . 94 . 92			
9	-11/2	.47 6.50 17441.63 .65	24595. 79	24602. 22	24608. 71				24691. 03 . 02 . 02	24698. 06 . 05 . 04				
	-21/2	6. 17435.19 . 18	24602. 23	24608. 66				1	24697. 47 . 49 . 44					
	$M_J =$	Magnetic level	42037. 42 . 41 6. 43	42043. 85 . 84 6. 50	0½ 42050. 34 . 34 6. 54	42056.90 .88 6.62	42063. 51 . 50 . 6. 67	42070. 18 . 17	42132. 66 . 67 7. 03	42139. 69 . 70 7. 39	42147. 07 . 09 7. 70	42154. 82	0½ 42192. 41 . 45 . 13, 10	01% 42205 59
	Ms		$[-2\frac{1}{2}]$	-11/2	-01/2	01/2	11/2	23/2	$[-1\frac{1}{2}]$	-01/2	03/2	11/2	, -01/2	%0
	No field level				z ⁶ D ² ½ 42053.73					6	2 °D'15, 42143.57		2 6D _{0.5} 42198 56	14100.00

Table 6. Asymmetric Zeeman patterns in multiplets a \$D-z Do and a D-z Fo of Mn I (field 84,700 oersteds)—Continued

			a	6D _{2½} =17451.52	2				a 6D11/4=	$a ^{6}\mathrm{D}_{152} = 17563.48$		a 6Do1/2=	=17637.15
$M_J = = -2\frac{1}{2}$ $-1\frac{1}{2}$ $R_J = -1\frac{1}{2}$	-142 6 17 6	-11/2		50 -01/2	01/2	11/2 6 67	21/2	$-1\frac{1}{2}$	-01/2	01/2	11/2	-01/2	01/2
17441. 63 . 65	0.40 17441. 63 . 65	17441. 63 . 65	ne	17448.15 .15	17454. 71	17461.29	17467.95	17557. 52	17564. 63	17572.01	17559. 69	17630.91	17644.09
2½ 43582. 71 26147. 52 26141. 08 . 71 . 53 06 4. 85 49*	26141.	26141.						26025. 18 . 18					T
-1½ 43587. 58 26152. 39 26145. 95 261 56 5. 05 . 49*	26145.95	26145.95	261	26139. 43 . 41 . 36				26030. 05 . 03 . 05	26022. 95 . 94 . 93				
0½ 43592. 61 · 61 · 61 · 61 · 61	96	96	261	26144, 46 . 46 . 37*	26137. 90 . 90 . 89			26035. 09 . 08 . 07	26027. 98 . 99 . 98	26020. 60 . 60 . 62			
0½ 43597. 81 . 79 . 5. 35	361	261	261	26149. 66 . 64 . 64	26143. 10 . 08 . 05	26136. 52 . 49 . 47			26033.18 .17	26025. 80 . 78 . 75	26018. 12 . 11		
1½ 42603. 18 5. 51					26148. 47 . 43 . 45	26141. 89 · . 84 80	26135. 23 . 17 . 17			26031. 17 . 13	26023, 49 . 46 . 46		
2½ 43608.69						26147. 40 . 35 . 41	26140. 74 . 68 . 70				26029. 00 8. 97 8. 95		
1.1½ 43638, 58 26203, 39 26196, 95 26190, 42 . 42 . 41 . 94 94 42	26196. 95 . 94 . 94	95 94 94	26190	. 43] L I I I I I I I I I	26081. 05 . 06 . 06	26073. 95 . 97 74. 00			26007. 67 . 65 . 65	
0½ 43641. 81	. 32	. 32	26193.	66 82 82 82	26187. 10 . 26 . 25			26084. 25 . 44 . 44	26077. 18 . 35 . 34	26069. 80 . 96 . 96*		26010. 90 11. 03 11. 02	25997. 72 . 86 . 85
0½ 43646. 03	26197	26197	26197		26191. 32 . 24 . 24	26184. 74 . 65 . 65			26081, 40 . 33 . 28*	26074. 02 3. 94 3. 94	26066. 34 . 27 . 36	26015. 12 . 01 4. 97	26001. 94 . 84 . 82
13/2 43651. 24				1 1 1	26196. 53 . 54 . 56	26189. 95 . 95 . 94	26183. 29 . 28 . 29			26079. 23 . 24 . 26	26071. 55 . 57 . 57		26007. 15 . 14 . 14
0½ 43675. 50								26117. 97 . 79 . 83	26110. 87 . 70 . 70	26103. 49 . 31 . 30		26044. 59 . 38 . 36	26031. 41 . 21 . 20
0)½ 43672. 86				1 1 1 2 1 1 1 1 1 1 1				F J 1 1	26108. 23 . 32 . 29	26100.85 . 93 . 92	26093. 17 . 26 . 27	26041. 95 2. 00 2. 03	26028. 77 . 83 . 83

great differences that exist between values for perturbed and for unperturbed levels (compare cols. 7 and 8 of table 5). This proves that the approximate theory of the Paschen-Back effect applies closely to the asymmetrical patterns of the spectrum Mn I. There are, however, a few cases in which the differences between observed and calculated values, for the magnetic levels, exceed the expected errors of measurement. The most important cases are the following (see table 7).

All the components having origins in these levels show, as may be seen in table 6, very great differences between calculated and observed wavenumbers. It is to be noted that all these components have origin in levels with magnetic quantum numbers $M=\pm 0\frac{1}{2}$. We shall consider this problem in the next paragraphs.

Table 7. Magnetic levels with strong perturbations in Mn i

		Level	
Designation	Calculated	Observed	Observed -calculated
$z^{6}\mathrm{D}_{0\frac{14}{2}}^{-0\frac{14}{2}}$	42192. 41	. 45	0. 04
$z^{6}\mathrm{D}_{0\%}^{0\%}$	42205. 59	. 55	-0.04
z 6F-01/4	43641. 81	. 97	0. 16
z 6F012	43646. 03	5. 95	-0.08
z 6F-016	43675. 50	. 32	-0.18
2 6 F 0 12	43672. 86	. 94	0. 08

7. Computation of g-Values From the Level Values

In the preceding discussion we have seen that, with few exceptions, the calculated values are closely coincident with the observed, showing that the theory is valid for these cases of manganese. It may be recalled now that eq 15 of this theory, which gives the separation between pairs of magnetic levels with the same absolute M-value but different sign, is independent of the quadratic terms, and hence that equal separations are obtained for perturbed and for unperturbed levels. This means that it will be possible to eliminate distortion due to weak Paschen-Back interaction by using eq 15. Solving eq 15 we have

$$g_J = \frac{\Delta T'^{-M, +M}}{2M_J a} \tag{23}$$

which gives the g-value corresponding to each pair of magnetic levels T'^{-M} and T'^{+M} . This formula indicates that to obtain a g-value it is only necessary to divide the separation between the two levels involved by $2M_Ja$. As an example the g-value corresponding to the observed magnetic levels 17435.18 $(M=-2\frac{1}{2})$ and 17467.97 $(M=+2\frac{1}{2})$, a being equal to 3.955, may be calculated as

$$\frac{17467.97 - 17435.18}{2 \times 2 \% \times 3.955} = 1.658.$$

In table 5, last column, the g-values computed in this way for each pair $\pm M$ are listed in front of the corresponding (-M)-values.

8. Computation of g-Values From the Observed Components of Patterns

It is interesting now to compute g-values directly from the observed patterns and to compare the resulting values with those derived from levels that were given in table 5. Table 8 shows details of the calculation. In the first column are given the wavelengths and transitions of the spectroscopic lines. In the second are listed the polarizations of the magnetic components whose wave numbers are in column 3. Lines marked with (*) are poorly measured.

In order to eliminate the distortions due to partial Paschen-Back effect the separations are taken, as indicated by eq 21 and 22 between components of the same order on both sides of the line without field. These separations are written after the components of smaller wave number. Thus, the difference between the lines 24477.18 and 24492.84 is written after the former. The separations, which are given in cm⁻¹, are divided by $2a=2\times3.955=7.910$ to obtain the components of the pattern in Lorentz units. These resultant components are listed in column 5. As usual, parallel components are given in parentheses.

The next step is to calculate the mean values of the intervals between adjacent components of a pattern. The intervals are given in column 6, and at the bottom of each set of intervals is written their mean value. The last interval in each set is the double value of the smallest parallel component, which itself is an interval.

In table 8 the intervals in each pattern are so closely equal that accurate mean values have been obtained. Each normal component and the mean interval provide two equations for calculating the g-values of the two levels involved. The resulting g-values are written after the respective normal component. Thus, the first component in table 8, namely 1.980, with the mean interval 0.212 gives the two g-values 1.874 for a $^6D_{1/2}$ and 1.662 for z $^6D_{21/2}$

There are three lines 3843, 3833, and 3816 A whose intervals, within each pattern, are very different and hence have not been included in table 8. The line 3816 A, for example, has the following components and intervals:

Components 2. 544 1. 987 1. 334 0. 775 (0. 885) (0. 3: Intervals 0. 557 0. 653 0. 559 0. 653 0. 559

The impossibility of deriving an accurate mean value, for the interval, with values such as 0.557 and 0.653 is evident.

Recently, Catalán and Velasco have shown, [8] and [9], that in cases such as these it is, nevertheless, possible to obtain g-values from the components if these are treated in separate groups, one for each

Table 8. Asymmetric patterns in Mn I [Field 84,700 oersteds; LU $3.955~\mathrm{cm}^{-1}$]

Spectroscopic transition and wavelength	Polariza- tion	Observed pattern	Separation (cm ⁻¹)	Component	Interval	g-val	lues
$a~^6\mathrm{D}_{154} - z~^6\mathrm{D}_{254}^2 \ 4082.945\mathrm{A}$	σ σ σ σ π π π σ σ σ σ σ σ σ σ σ σ σ σ σ	24477. 18 24478. 32 24479. 21 24479. 88 24483. 83 24484. 88 24485. 25 24486. 32 24490. 49 24491. 49 24492. 23	15. 66 13. 91 12. 28 10. 61 2. 49 0. 84	1. 980 1. 759 1. 552 1. 339 (0. 314) (0. 106) Mean	0. 221 0. 207 0. 213 0. 208 0. 212 0. 212	a ⁶ D1½ 1. 874 1. 865 1. 870 1. 869	z 6 D $_{2}^{9}$ / $_{2}$ 1 6 62 2 1 6 53 2 6 58 3 6 58
$a~^{6}\mathrm{D}_{094}-z~^{6}\mathrm{D}_{194}^{\circ} \ 4079.415\mathrm{A}$	$\left\{\begin{array}{c} \sigma \\ \sigma \\ \sigma \\ \pi \\ \pi \\ \sigma \\ \sigma \end{array}\right.$	24492. 84 24495. 58 24501. 77 24503. 00 24506. 34 24508. 75 24510. 70 24516. 15	20. 57 8. 93 5. 75	2. 600 1. 129 (0. 727) Mean	1. 471 1. 454 1. 463	3. 331 3. 322 a ⁶ D _{0½}	z 6D ₀₄ 1. 869 1. 860
$a~^{6}\mathrm{D}_{014} - z~^{6}\mathrm{D}_{014}^{\circ} \ 4070.280\mathrm{A}$	$\left\{\begin{array}{c}\sigma\\\pi\\ \pi\\ \sigma\end{array}\right.$	24548. 33 24561. 43* 24561. 42 24561. 43* 24574. 64	26. 31 0. 00	3. 325 (0. 000)		3. 325*	3. 325*
$a~^{6}\mathrm{D}_{194}-z~^{6}\mathrm{D}_{094}^{8} \ 4058.936\mathrm{A}$	$ \begin{cases} \sigma \\ \sigma \\ \pi \end{cases} $ $ \pi \\ \sigma \\ \sigma $	24620. 42 24625. 87 24627. 84 24630. 08 24633. 54 24634. 93 24640. 91	20. 49 9. 06 5. 70	2. 590 1. 145 (0. 721) Mean	1. 445 1. 442 1. 444	a ⁶ D ₁₅₄ 1. 868 1. 867	z ⁶ D _{0½} 3. 312 3. 311
a ⁶ D _{2½} – z ⁶ D ⁶ ½ 4048.747A	σσσσππππσσσσσσσσσσσσσσσσσσσσσσσσσσσσσ	$\begin{array}{c} 24684.\ 54\\ 24685.\ 02\\ 24685.\ 79\\ 24686.\ 84\\ 24691.\ 02\\ 24691.\ 55\\ 24692.\ 05\\ 24692.\ 39\\ 24693.\ 50\\ 24697.\ 44\\ 24698.\ 04\\ 24698.\ 92\\ 24700.\ 06\\ \end{array}$	15, 52 13, 90 12, 25 10, 60 2, 48 0, 84	1. 962 1. 757 1. 549 1. 341 (0. 314) (0. 106) Mean	0. 205 0. 208 0. 208 0. 208 0. 212 0. 208	$egin{array}{c} a^{-6} D_{234} \\ 1, 650 \\ 1, 653 \\ 1, 653 \\ 1, 652 \\ \end{array}$	z ⁶ D ₁ , 4 1, 858 1, 861 1, 861 1, 860
$a~^6\mathrm{D}_{112}-z~^6\mathrm{F}_{212}^2 \ 3841.~074\mathrm{A}$	σ σ σ σ π π π σ σ σ σ σ σ σ σ σ σ σ σ σ	26018. 10 26020. 62 26022. 93 26025. 18 26023. 46 26025. 75 26027. 98 26030. 05 26038. 95 26031. 13 26033. 15 26035. 07	16. 97 12. 53 8. 20 3. 77 6. 59 2. 23	2. 145 1. 584 1. 037 0. 477 (0. 833) (0. 282)	0. 561 0. 547 0. 560 0. 551 0. 564 0. 556	a ⁶ D _{11/2} 1. 867 1. 862 1. 871 1. 867	z °F ₂₁₆ 1. 311 1. 306 1. 315 1. 311

Table 8. Asymmetric patterns in Mn I—Continued [Field 84,700 oersteds; LU 3.955 cm-1]

Spectroscopic transition and wavelength	Polariza- tion	Observed pattern	Separation (cm ⁻¹)	Component	Interval	<i>g</i> -v	alues
$a~^{6}\mathrm{D}_{154}-z~^{6}\mathrm{F}_{054}^{\circ}\ 3839.779\mathrm{A}$	$ \begin{cases} \sigma \\ \pi \end{cases} $	26031, 20 26028, 83 26035, 81 26044, 36 26042, 03	10. 83 15. 53	1, 369 (1, 963)		<i>a</i> ⁶ D ₀ , 4 3. 332	$-rac{z^{6} ext{F}_{014}^{8}}{-0.594}$
$a\ ^{6}\mathrm{D}_{154}-z\ ^{6}\mathrm{F}_{054}^{\circ}\ _{3829.679\mathrm{A}}$	$\left\{\begin{array}{c}\sigma\\\sigma\\\pi\\\pi\\\sigma\\\sigma\end{array}\right.$	26093. 27 26103. 30 26100. 92 26104. 47 26110. 70 26108. 29 26117. 83	24. 56 4. 99 9. 78	3. 105 0. 631 (1. 236)	2. 474 2. 472 2. 473	a ⁶ D _{1½} 1. 868 1. 867	$z^{6}\mathrm{F}_{014}^{\circ}$ -0.606 -0.605
$a^6\mathrm{D}_{234} \!-\! z^6\mathrm{F}_{234}^\circ \\ 3823.891\mathrm{A}$	σ σ σ π π π π σ σ σ σ σ σ σ σ σ σ σ σ σ	26135. 17 26136. 47 26137. 89 26139. 36 26141. 15* 26140. 70 26141. 80 26143. 05 26143. 98 26144. 37* 26145. 26147. 49* 26147. 41 26148. 45 26149. 64 26150. 26152. 49*	17. 32* 11. 75 9. 09 6. 26* 6. 79* 1. 32*	2. 190 1. 485 2. 149 0. 791 (0. 858) (0. 167) Mean	0. 352* 0. 353* 0. 336 0. 358 0. 345* 0. 346* 0. 334	a ⁶ D _{2½} 1. 671* 1. 658 1. 668 1. 656*	z ⁶ F _{3/3} 1. 325* 1. 312 1. 322 1. 310*

pair of magnetic levels $\pm M$. Table 9 shows the calculation of g-values by that method for the three lines mentioned above. The general arrangement of table 9 is similar to that of table 8, but the components have been placed in two groups. It has been possible to obtain the g-values for the two levels involved in all cases except one, that of the component -0.064, because in this case the interval is unknown. The g-value of one of the levels involved, namely 3.328 for $a^6D_{0\frac{1}{2}}$, has been adopted, and then the g-value for the other level has been derived. Table 9 shows that the g-values obtained for $a^6D_{0\frac{1}{2}}$, $a^6D_{1\frac{1}{2}}$, and $a^8D_{0\frac{1}{2}}$ are closely coincident with those obtained in table 8, thereby justifying the method of Catalán and Velasco.

It is to be noted that the g-values obtained for the same spectroscopic level, in different patterns, are practically identical. Very accurate mean values may be derived from the data of tables 7 and 8. The resulting values have been compiled in table 10.

The agreement between values derived from levels or from components is extremely good. This is a proof of the validity of both methods of deriving g-values. The method of levels, although a little more difficult to apply, is the more general, for it gives results in all cases. The method of the components is, however, much more simple and is the one usually employed by all observers of the Zeeman

effect; but it must be applied with caution because in some asymmetric patterns it may give less accurate g-values. The method of Catalán and Velasco may serve in such cases to obtain more reliable values.

Most of the levels in table 10 have g-values equal to those of LS-coupling, but z $^6\mathrm{P}_{0\%}^{\circ}$, z $^6\mathrm{F}_{1\%}^{\circ}$, and z $^6\mathrm{F}_{0\%}^{\circ}$ constitute clear exceptions to the rule. These exceptions are just those derived from levels in table 7. The two magnetic levels z $^6\mathrm{D}_{0\%}^{\circ 1\%}$ and z $^6\mathrm{D}_{0\%}^{\circ 1\%}$ have been displaced unequally. The level with negative M-value has received a positive additional impulse of 0.04 cm⁻¹, and that with the positive value has received an additional negative push of 0.04 cm⁻¹. The distance between these two levels compared with the distance between the unperturbed levels is shortened by 0.08 cm⁻¹. Hence the corresponding g-factor is altered. The g-value for LS-coupling is 3.333, and the real value is 3.312. We cannot suggest the cause for this anomalous displacement.

The other cases are closely connected with each other, as Catalán and Velasco have shown, [9] and [7, p. 200]. The g-values that are obtained for the two pairs $M=\pm 1\frac{1}{2}$ and $M=\pm 0\frac{1}{2}$ for z ${}^{6}F_{1\frac{1}{2}}$ are quite different. The first pair gives exactly the LS-value, but the pair $M=\pm 0\frac{1}{2}$ gives 1.006, which is 0.061 LU smaller than the LS-value. The additional impulses

Table 9. Zeeman patterns of level z $^6F_{144}^{\circ}$ of Mn I [Magnetic field 84,700 oersteds; LU 3.955 cm⁻¹]

V-Market State Company		[magnetic neid		340, 130 0.000	cin -j		
Spectroscopic transi- tion and wavelength	Polariza- tion	Observed pattern	Separa- tion (cm ⁻¹)	Compo- nent	Interval	g-va	alues
	σ	26007. 65 26007. 30	- 0. 51	-0. 064		a ⁶ D ₀ 14 [3. 328]	$z^{6}F_{1\%}^{\pm 1\%}$ 1. 067
	σ	26007. 14					
$a^{6}\mathrm{D_{0\%}} - z^{6}\mathrm{F_{1\%}^{\circ}}$ 3843. 988A	σ	25997. 85 26001. 82	17. 12	2. 165		3. 328	$z^{6}F_{1\frac{1}{2}}^{\pm0\frac{1}{2}}$ 1. 002
3843. 988A	π	26007.30	9. 20	(1. 163)		7-	
	σ	26011. 02 26014. 97					
	σ	26074, 00	5. 26	0. 665		a ⁶ D ₁₁₄ 1. 865	$z^{6}F_{136}^{\pm 136}$ 1. 065
	π	26071. 57 26075. 97	9. 49	(1. 200)		1. 800	1. 065
	π σ	26081. 06 26079. 26					
	σ	26066. 36	10.00	0.005		4 000	z 6F 11/4
$a^{6}\mathrm{D_{1\%}} - z^{6}\mathrm{F_{1\%}^{\circ}}$ 3833. 865A	σ	26069. 96*	18. 08 11. 32*	2. 285 1. 431	0.854	1. 857 1. 860	1. 000 1. 003
	π	26073. 94 26075. 95	3. 40	(0.430)	0.860		
	π	26077. 34		Mean	0.857		
	σσ	26081. 28* 26084. 44					
					20	a 6D24	z 6F _{1%}
	σ σ	26183. 29 26190. 42	20. 12 6. 13	2. 544 0. 775	1. 769	1. 659 1. 660	1. 069 1. 070
	π	26189. 94 26192. 93	7. 00	(0.855)	1. 770		
	π	26196. 94	~ -	Mean	1. 770		
	σ	26196. 55		1/3 Mean	0. 590	(m. m)	z 6F ± 01/2
$a^{6}\mathrm{D}_{2\frac{1}{2}}-z^{6}\mathrm{F}_{1\frac{1}{2}}^{\circ}$ 3816. 746A	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	26203. 41 26184. 65	15. 72	1. 987		1 000	
0010. 11011	σ	26187. 25	10. 55	1. 334	0. 653	1. 660 1. 660	1. 007 1. 007
	π	26191. 24 26192. 93	2. 58	(0. 326)	0. 652		
	π	26193. 82		Mean	0. 653	No. on	
	σ σ	26197. 80 26200. 37					

Table 10. Mean g-values for levels of Mn I
[Magnetic field 84,700 oersteds]

Designation	g-values cor the ob	g-values for		
Dougland	Levels	Components		
a 6D ₂ 1/4 a 6D ₁ 1/4 z 6D ₂ 1/4 z 6D ₁ 1/4	1. 867 3. 330 1. 656	1. 658 1. 866 3. 328 1. 658 1. 861	1. 657 1. 867 3. 333 1. 657 1. 867	
$egin{array}{cccccccccccccccccccccccccccccccccccc$	3. 312 1. 312 1. 067 1. 006	3. 312 1. 314 1. 068 1. 004 -0. 602	3. 333 1. 314 1. 067 -0. 667	

0.16 and $-0.08 \,\mathrm{cm^{-1}}$, which $z^{\,6}\mathrm{F^{-0.56}_{132}}$ and $z^{\,6}\mathrm{F^{+0.56}_{132}}$ have received, make their distance shorter by a total amount of 0.024 cm⁻¹, which accounts for the change of 0.061 LU in the g-values.

The magnetic levels z ${}^6F^{-0}_{0}$ and z ${}^6F^{+0}_{0}$ have received extra displacements -0.18 and 0.08 cm $^{-1}$, respectively. In this particular case of ${}^6F_{0}$, on account of the fact that the g-value is negative, the magnetic level M=-0½ is smaller than M=+0½. Hence the distance between these magnetic levels has been shortened by a total amount of 0.26 cm $^{-1}$, and this accounts for the change of g-value from -0.667 (LS-coupling value) to -0.602.

There is a close connection between the changes in g-values experienced by $z^6 F_{11/2}^\circ$ and $z^6 F_{01/2}^\circ$. As Catalán and Velasco have shown, the sums of the g-values for LS-coupling and for the observed levels are the

same. The sum in LS-coupling amounts to 1.067 + (-0.667) = 0.400 and to 1.001 + (-0.602) = 0.399 for the perturbed levels. A clear explanation of this case has been given by these authors [7, p. 200].

9. Theoretical Computation of Line Strengths in Zeeman Patterns

The strength, S, of a line is defined as a quantity that must be multiplied by the fourth power of the frequency and by the number of atoms in any one of the initial states, in order to obtain the radiated energy [7, p. 200]. There is a possibility of comparing relative strengths with observed intensities because all the lines of a Zeeman pattern have closely the same frequency and are produced by close states that have practically the same excitation.

The strength S^M of a component in a Zeeman pattern depends on the strength S of the parent line through the equation

$$S^{M} = S \times K,$$
 (24)

in which K is a constant whose values depend on the J- and M-values of the initial levels as expressed in the following formulas:

Spectroscopic transition	Magnetic transition	K-values
	$\begin{cases} M \to M \\ M \to M \pm 1 \\ M \to M \\ M \to M \pm 1 \end{cases}$	$\begin{array}{c} 2A(J^2-M^2)/J(2J-1) \\ (2J+1) \\ (1/2)A(J\mp M)(J\mp M-1)/\\ J(2J-1)(2J+1) \\ 2AM^2/J(J+1) & (2J+1) \\ (1/2)A(J\mp M) & (J\pm M-1) \\ J(J+1) & (2J+1) \end{array}$

Table 11. K- and (K)1/2-values for components in a Zeeman pattern

		/ TABLE 11. I	[Upper figure	s are <i>K</i> -values; low	$\operatorname{ver}(K)^{1/2}$ -values]			
			Odd mul	tiplicities, parallel	components			
	1	M=-3	_2	-1	0	+1	+2	+3
J	J -1	M=-3	-2	-1 /	0	+1	+2	+3
1	0	{			50. 00 7. 07			
2	1	{		15. 00 3. 87	20. 00 4. 47	15. 00 3. 87		
3	2	{	7. 14 2. 67	11. 43 3. 38	12. 86 3. 58	11. 43 3. 38	7. 14 2. 67	
4	3	\{\begin{array}{c} 4.16 \\ 2.04 \end{array}\end{array}\rightarrow{\text{\chi}}	7. 14 2. 67	8. 93 2. 99	9. 5 <mark>2</mark> 3. 09	8. 93 2. 99	7. 14 2. 67	4. 16 2. 04
	J 1	-		25. 00 5. 00	0, 00 0. 00	25. 00 5. 00		==
2	2	{	20. 00 4. 47	5. 00 2. 24	0. 00 0. 00	5. 00 2. 24	20. 00 4. 47	
3	3	{ 16. 07 4. 01	7. 14 2. 67	1. 79 1. 29	0. 00 0. 00	1. 79 1. 29	7. 14 2. 67	16. 07 4. 01

Table 11. K- and $(K)^{1/2}$ -values for components in a Zeeman pattern—Continued [Upper figures are K-values; lower $(K)^{1/2}$ -values

			Odd m	ultiplicities, norma	l components			
J	J -1	M = -2	-1	0	+1	+2	+3	+4
		M-1 = -3	-2	-1	0	+1	+2	+3
1	0				25. 00 5. 00			Y == / ==
2	1		7	2. 50 1. 58	7. 50 2. 74	15. 00 3. 87		
3	2	{	0. 71 0. 84	2. 14 1. 46	4. 29 2. 07	7. 14 2. 67	10. 71 3. 27	,
4	3	0. 30 0. 55	0. 90 0. 95	1. 78 1. 33	2. 98 1. 73	4. 49 2. 12	6. 25 2. 50	8. 33 2. 89
J	J							
1	1	{		12. 50 3. 54	12. 50 3. 54			
2	2	{	5. 00 2. 24	7. 50 2. 74	7. 50 2. 74	5. 00 2. 24		
3	3	2. 68 1. 64	4. 46 2. 11	5. 35 2. 31	5. 35 2. 31	4. 46 2. 11	2. 68 1. 64	

17								8 11 11 11	
			Even n	nultiplicities, p	arallel componer	nts			
J	J–1	$M = -3\frac{1}{2}$ $M = -3\frac{1}{2}$	$-2\frac{1}{2} \\ -2\frac{1}{2}$	$-1\frac{1}{2}$ $-1\frac{1}{2}$	$-0\frac{1}{2}$ $-0\frac{1}{2}$	$+0\frac{1}{2} + 0\frac{1}{2}$	+1½ +1½	$+2\frac{1}{2} + 2\frac{1}{2} + 2\frac{1}{2}$	$+3\frac{1}{2} + 3\frac{1}{2}$
1½	01/2	{			25. 00 5. 00	25. 00 5. 00	 		
2½	1½	{	-	10. 00 3. 16	15. 00 3. 87	15. 00 3. 87	10. 00 3. 16		
3½	2½	{ ==	5. 36 2. 32	8. 93 2. 99	10. 71 3. 27	10. 71 3. 27	8. 93 2. 99	5. 36 2. 32	
4½	3½	3. 33 1. 82	5. 83 2. 41	7. 50 2. 74	8. 33 2. 89	8. 33 2. 89	7. 50 2. 74	5. 83 2. 41	3. 33 1. 82
J	J								
0½	0½	=-			25. 00 5. 00	25. 00 5. 00			
1½	1½	{		22. 50 4. 74	2. 50 1. 58	2. 50 1. 58	22. 50 4. 74		
2½	$2\frac{1}{2}$	{ ==	17. 85 4. 22	6. 43 2. 54	0. 71 0. 84	0. 71 0. 84	6. 43 2. 54	17. 85 4. 22	
3½	3½	{ 14. 60 3. 82	7. 45 2. 73	2. 68 1. 61	0. 30 0. 55	0. 30 0. 55	2. 68 1. 61	7. 45 2. 73	14. 60 3. 82

Table 11. K- and (K)^{1/2}-values for components in a Zeeman pattern—Continued [Upper figures are K-values; lower (K)^{1/2}-values]

			Even r	nultiplicities, no	ormal componen	ts			
J	J-1	$M = -2\frac{1}{2}$	-11/2	$-0\frac{1}{2}$	$0\frac{1}{2}$	1½	2½	$3\frac{1}{2}$	4½
9		$M = -3\frac{1}{2}$	$-2\frac{1}{2}$	$-1\frac{1}{2}$	$-0\frac{1}{2}$	0½	1½	$2\frac{1}{2}$	3½
1½	0½	\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \			6. 25 2. 50	18. 75 4. 33	00 00 00 00		
$2\frac{1}{2}$	1½	{		1. 25 1. 12	3. 75 1. 94	7. 50 2. 74	12. 50 3. 54		
3½	$2\frac{1}{2}$	{	0. 45 0. 67	1. 34 1. 16	2. 68 1. 64	4. 46 2. 11	6. 70 2. 50	9. 37 3. 06	
$4\frac{1}{2}$	$3\frac{1}{2}$	$ \begin{cases} & 0.21 \\ & 0.46 \end{cases} $	0. 63 0. 79	1. 25 1. 12	2. 08 1. 44	3. 12 1. 77	4. 37 2. 09	5. 83 2. 41	7. 50 2. 74
J	J								
0½	0½				25. 00 5. 00				
1½	1½	{		7. 50 2. 74	10. 00 3. 16	7. 50 2. 74			
$2\frac{1}{2}$	$2\frac{1}{2}$		3. 57 1. 89	5. 71 2. 39	6. 43 2. 54	5. 71 2. 39	3. 57 1. 89		
$3\frac{1}{2}$	3½	$ \left\{ \begin{array}{c} 2.08 \\ 1.44 \end{array} \right. $	3. 57 1. 89	4. 46 2. 11	4. 76 2. 18	4. 46 2. 11	3. 57 1. 89	2. 08 1. 44	

The value J is the larger of two J-values involved. For these equations it has been assumed that the observations have been made perpendicularly to the magnetic field. K-values have been computed by means of these equations and are given in table 11. The value 75 has been assigned to constant A so that the sum of all parallel components in a pattern may be 50 and that the corresponding sum for each of the two groups of normal components may be 25. Thus the sum of all components in each pattern will be 100.

In calculations related to the strength of lines the square root $(S)^{1/2}$ of S is more convenient than the strength itself for comparison with the observed intensities. Accordingly, we have computed the square roots of the K-values. In table 11 the square roots are given under their respective S-values. Taking the square root of both members of eq 24, we have

$$(\mathbf{S}^{\scriptscriptstyle M})^{\scriptscriptstyle 1/2} = \mathbf{S}^{\scriptscriptstyle 1/2} \times K^{\scriptscriptstyle 1/2}. \tag{25}$$

This equation means that to obtain $(S^M)^{\frac{1}{2}}$ -values it is only necessary to multiply the values of $K^{\frac{1}{2}}$ by the strengths of their respective spectroscopic lines. The quantities $(S^M)^{\frac{1}{2}}$, $S^{\frac{1}{2}}$, and $K^{\frac{1}{2}}$ are either positive or negative. The sign of $(S^M)^{\frac{1}{2}}$ depends on the sign of $S^{\frac{1}{2}}$ and $K^{\frac{1}{2}}$. The sign of $S^{\frac{1}{2}}$ depends on the changes of the L- and J-values in the spectral line. The sign of $K^{\frac{1}{2}}$ depends on the changes in the J- and M-values for the magnetic levels of the components. Tables 12 and 13 give the signs for the different cases.

Table 12. Signs of S^{1/2} (spectral lines)

Quantum numbers	<i>J</i> → <i>J</i> +1	$J\!\!\to\!\! J$	$J \rightarrow J-1$
$L \rightarrow L + 1$	+	+	_
$L \rightarrow L$	_	a <u>+</u>	-
$L \rightarrow L-1$		+	+

a Sign (+) if S(S+1) < L(L+1) + J(J+1); sign (-) if S(S+1) > L(L+1) + J(J+1). Here S is not the strength of the line, but is the resultant spin.

Table 13. Signs of K^{1/2} (magnetic components)

Quantum numbers	$M \rightarrow M+1$	$M \rightarrow M$	$M \rightarrow M-1$
$J \rightarrow J + 1$	_	+	+
$J \rightarrow J$	+	a <u>+</u>	+
$J \rightarrow J-1$	+	+	_

• The same sign as M.

10. Theoretical Strengths $(S^M)^{1/2}$ of Components in Patterns of a Multiplet $^6\mathrm{D} - ^6\mathrm{F}^\circ$

The strengths may be computed by formula (25). The S-values for lines in a multiplet ${}^6D - {}^6F^{\circ}$ can be deduced by the classical formulas of Kronig, of Sommerfeld and Hönl, and of Russell [10]. The square roots of the values obtained are given in table 14. The signs have been computed by table 12.

In order to compute the final $(S^M)^{\frac{1}{2}}$ -values we have multiplied, for each pattern, the strengths of its components, given in table 11, by the strength of the line

Table 14. Values of S^{1/2} for ⁶D - ⁶F° lines

Levels	6D _{4½}	6D _{3½}	6D2½	6D1½	6D0½
6F° 5½ 6F° 4½	18. 97 7. 45	15. 63			
6F°31/2	-2.11	9.02 -3.21	12. 42		
6F°2½ 6F°1½		- 3. 21	9. 13 -3. 79	9. 30 8. 26	6. 11
6F°01/2				-3.65	6. 83

without field, given in table 14. The resulting values are given in table 15.

11. Theoretical Computation of Line Strengths in a Zeeman Pattern Perturbed by Partial Paschen-Back Effect

The partial Paschen-Back effect, in LS-coupling, produces intensity distortions in the component lines of the patterns. These distortions may be calculated by the so-called second-order perturbation theory. In this theory two magnetic levels

 T_J^M and T_{J-1}^M belonging to consecutive spectroscopic levels T_J and T_{J-1} of a term T, and having the same M-value, interact with each other, perturbing mutually the strengths of their combinations with another third level. If we set $T_J^M < T_{J-1}^M$ —the third level being inappreciably lower or higher than the other two—the perturbed strengths of the transitions are given by eq 26a and b, which we take from Kiess and Shortley [7, p. 204]

pert.
$$(S_J^M)^{\frac{1}{2}}$$
 = unpert. $(S_J^M)^{\frac{1}{2}}$ —
$$(aI/\Delta) \text{ unpert.}(S_{J-1}^M)^{\frac{1}{2}}, \qquad (26a)$$

pert.
$$(S_{J-1}^M)^{\frac{1}{2}} = \text{unpert.}(S_{J-1}^M)^{\frac{1}{2}} + (aI/\Delta) \text{ unpert.}(S_J^M)^{\frac{1}{2}}.$$
 (26b)

The first members of these equations are the strengths of the perturbed transitions. The quantity a is the LU in cm⁻¹ for the magnetic field, I is the interaction factor given in table 3, and Δ the distance, in cm⁻¹, between the two interacting magnetic levels. The remaining factors are the strengths of

Table 15. Calculated strengths in multiplet a ^6D-z $^6F^\circ$ of Mn I with and without perturbation [Magnetic field 84,700 oersteds. Upper figures are values without perturbation.]

							Design	nation					
Designation				a 61)21/2				a 61)11/4		a ⁶ I	001/2
	M	$-2\frac{1}{2}$	-11/2	-01/2	01/2	1½	21/2	-11/2	$-0\frac{1}{2}$	0½	1½	$-0\frac{1}{2}$	0½
	$ -2\frac{1}{2}$	$\begin{cases} -38.5 \\ -37.1 \end{cases}$	17. 3 17. 4	/				32. 9 33. 5					
	$-1\frac{1}{2}$	17. 3 17. 8	$ \begin{array}{r} -23.2 \\ -20.6 \end{array} $	23. 7 24. 1				29. 4 32. 4	25. 5 24. 3				
$\left. egin{array}{c} z {}^{_{6}}\mathrm{F}_{212}^{_{2}} \end{array} ight -0lag{1}{2} ight $	{	23. 7 24. 0	$ \begin{array}{c c} -7.7 \\ -4.6 \end{array} $	23. 2 23. 2			$-10.4 \\ -12.3$	36. 0 37. 2	18. 0 15. 9				
2 -1 21/2	01/2	{ 		23. 2 23. 1	7. 7 10. 7	23. 7 23. 3			$-18.0 \\ -20.2$	36. 0 34. 8	10. 5 8. 5		
	$1\frac{1}{2}$.		 		23. 7 23. 2	23. 2 25. 8	17. 3 16. 7			$ \begin{array}{r} -25.5 \\ -26.7 \end{array} $	29. 4 26. 4		
	$2\frac{1}{2}$					17. 3 16. 6	38. 5 40. 0				-32.9 -32.4		
	$-1\frac{1}{2}$	$\begin{cases} -18.4 \\ -11.8 \end{cases}$	$-12.0 \\ -12.9$	4. 2 5. 6				-39.2 -36.7	22. 6 23. 4	00 ou		26. 5 27. 1	
z ⁶ F ₁ ,	$-0\frac{1}{2}$		$-10.4 \\ -8.3$	-14.7 -15.0	7. 4 9. 0			22. 6 24. 3	$-13.1 \\ -7.8$	26. 1 25. 8		30. 6 36. 7	15. 3 10. 1
	0½		Service (Marie	$ \begin{array}{r} -7.4 \\ -5.7 \end{array} $	$-14.7 \\ -14.3$	10. 4 12. 4			26. 1 26. 6	13. 0 18. 3	22. 6 20. 9	-15.3 -21.5	30. 6 24. 4
	1½				$ \begin{array}{c} -4.2 \\ -2.9 \end{array} $	-12.0 -11.0	13. 4 15. 1			22. 6 21. 9	39. 2 41. 6		-26.5 -24.8
z ⁶ F _{01/2}	$\int -0\frac{1}{2} \cdot$							-15.8 -11.1	-18.3 -18.5	9. 1 12. 1		-34.2 -29.1	34. 2 38. 0
7/2	$\begin{cases} -0\frac{1}{2} \\ 0\frac{1}{2} \end{cases}$	{							$ \begin{array}{r} -9.1 \\ -6.2 \end{array} $	-18.3 -18.0	15. 8 20. 5	34. 2 30. 3	$\frac{34.2}{39.2}$

Interacting levels	Interval		<i>I</i> -values		aI/Δ			
		$M = \pm 0\frac{1}{2}$	1½	21/2	$M = \pm 0\frac{1}{2}$	11/2	2½	
a ⁶ D _{3½} , a ⁶ D _{2½}	169. 52	1, 050	0, 959	0, 742	0. 025	0. 022	0. 017	
a 6D ₂₁₆ , a 6D ₁₁₆	116. 96	1. 200	0. 989		0. 041	0. 033		
$a {}^{6}\mathrm{D}_{1\frac{1}{2}}, a {}^{6}\mathrm{D}_{0\frac{1}{2}}$	68. 67	1. 247			0, 072	4_		
z 6F31/2, z 6F21/2	71. 42	1. 355	1. 258	0. 958	0. 075	0.070	0.053	
z 6F° 21/2, z 6F° 1/2	48. 95	1. 470	1. 200	PT 50	0. 119	0. 097	-	
z 6F° 11/4, z 6F° 1/4	28. 51	1. 490	7.0		0. 207			

the unperturbed transitions. For a component perturbed by two others the changes are additive. Special care must be given in these calculations to the signs of the strengths.

12. Perturbations in the Strengths of the Components in Some Patterns of Mn I

We are now prepared to compare the observed intensities in some patterns of Mn I with the theoretical strengths computed by eq 26a and b. For this comparison we have selected the multiplet $a^6D-z^6F^\circ$ for two reasons. First, this multiplet has an outstanding intensity, making it easy to observe all the components of the patterns, even the faintest. Second, the I factors for such terms have high values (see table 3) especially for the lower J-values of z 6F $^\circ$, and the separations Δ are relatively small, so that the magnitudes of I/Δ are very important.

First we have computed the values of aI/Δ for the different transitions in this multiplet. Only the values corresponding to small J-values have been considered. Within the accuracy of this calculation the separation between spectroscopic levels may be used instead of that between magnetic levels belonging to the spectroscopic levels. Values of separations have been taken from table 4 and I-values from table 3. For the LU, a=3.955 has been used. The

resulting values are given in table 16. We shall proceed now to compute independently the levels of a D and z Fo. A few examples will illustrate in detail how these calculations have been made.

We select first a very simple case, that of the component a ${}^{6}D_{0}^{0}{}^{1}_{2} - z$ ${}^{6}F_{0}^{0}{}^{1}_{2}$. Its initial state a ${}^{6}D_{0}^{0}{}^{1}_{2}$ is perturbed only by a ${}^{6}D_{0}^{0}{}^{1}_{2}$, and its final state z ${}^{6}F_{0}^{0}{}^{1}_{2}$ only by z ${}^{6}F_{0}^{0}{}^{1}_{2}$. The strengths of the unperturbed transitions involved, taken from table 15 (in the table the values are rounded) are

$$a^{6}\mathrm{D}_{0\frac{1}{2}}^{0\frac{1}{2}} \rightarrow z^{6}\mathrm{F}_{1\frac{1}{2}}^{0\frac{1}{2}} = 30.55$$

$$a \, {}^{6}\mathrm{D}_{1\frac{1}{2}}^{0\frac{1}{2}} \rightarrow z \, {}^{6}\mathrm{F}_{0\frac{1}{2}}^{0\frac{1}{2}} = -18.25$$
 $a \, {}^{6}\mathrm{D}_{0\frac{1}{2}}^{0\frac{1}{2}} \rightarrow z \, {}^{6}\mathrm{F}_{0\frac{1}{2}}^{0\frac{1}{2}} = 34.15$

Factors aI/Δ taken from table 16 are: 0.207 for the influence of $z^{6}F_{1\frac{1}{2}}^{0\frac{1}{2}}$, $z^{6}F_{0\frac{1}{2}}^{0\frac{1}{2}}$, and 0.072 for that of $a^{6}D_{1\frac{1}{2}}^{0\frac{1}{2}}$, $a^{6}D_{0\frac{1}{2}}^{0\frac{1}{2}}$. The values of the perturbations will then be:

$$0.207 \times 30.55 = 6.32$$
 and $0.072 \times (-18.25) = -1.31$.

The first is to be added (eq 26a) because it is due to the influence of level z ${}^{6}F_{11/2}$ on another *higher* level z ${}^{6}F_{01/2}$. The second perturbation also is to be added because it is due to the influence of level a ${}^{6}\mathrm{D}_{1}$ on another higher one, a ${}^{6}\mathrm{D}_{0}$. Hence the final value of the perturbed strength will be 34.15+ 6.32 - 1.31 = 39.16.

The line $a^{6}D_{1\frac{1}{2}}^{0\frac{1}{2}} \rightarrow z^{6}F_{1\frac{1}{2}}^{0\frac{1}{2}}$ is a more complicated experience. ample. Its initial state is affected by both $a \, ^6\mathrm{D}_{344}^{042}$ and $a^6 D_{0\frac{1}{2}}^{0\frac{1}{2}}$. Its final state is perturbed by $z^6 F_{0\frac{1}{2}}^{0\frac{1}{2}}$ and $z^6 F_{0\frac{1}{2}}^{0\frac{1}{2}}$. The strengths without perturbation of the strength perturbations under the influence of | the components (see table 11) are

$$a\ ^6\mathrm{D}_{1\frac{1}{2}}^{0\frac{1}{2}}\!\!\to\!\!z\ ^6\mathrm{F}_{2\frac{1}{2}}^{0\frac{1}{2}}\!\!=\!35.99$$

$$a\ ^6\mathrm{D}_{2\frac{1}{2}}^{0\frac{1}{2}}\!\!\to\!\!z\ ^6\mathrm{F}_{1\frac{1}{2}}^{0\frac{1}{2}}\!\!=\!13.05 \qquad a\ ^6\mathrm{D}_{0\frac{1}{2}}^{0\frac{1}{2}}\!\!\to\!\!z\ ^6\mathrm{F}_{1\frac{1}{2}}^{0\frac{1}{2}}\!\!=\!13.05$$

$$a\ ^6\mathrm{D}_{0\frac{1}{2}}^{0\frac{1}{2}}\!\!\to\!\!z\ ^6\mathrm{F}_{0\frac{1}{2}}^{0\frac{1}{2}}\!\!=\!13.25$$

The values of aI/Δ , as given by table 13 are 0.041 and 0.072 for the influences of D_{234} , D_{134} , and D_{034} , D_{134} , respectively; and 0.119 and 0.207 for those of F_{234} , F_{134} and F_{034} , F_{134} , respectively.

The values of the perturbations are thus: 0.041×

(-14.67) = -0.60, $0.072 \times (30.55) = 2.20$, $0.119 \times (35.99) = 4.28$, and $0.207 \times (-18.25) = 3.78$. These perturbations will be added for D_{214} , D_{114} and for $F_{2\frac{1}{2}}$, $F_{1\frac{1}{2}}$; and subtracted for $D_{0\frac{1}{2}}$, $D_{1\frac{1}{2}}$ and for $F_{0\frac{1}{2}}$, $F_{1\frac{1}{2}}$ because of the relations $D_{2\frac{1}{2}} < D_{1\frac{1}{2}} < D_{0\frac{1}{2}}$ and $F_{2\frac{1}{2}} < F_{1\frac{1}{2}} < F_{0\frac{1}{2}}$. The final strength of the perturbed line will be 13.05 + (-0.60) - 2.20 + 4.38 - (-3.78) =18.31. Thus the line with strength 13.05 has been distorted, and its strength has been changed by

With the same procedure we have computed the perturbations for some other patterns of multiplet $a^6\mathrm{D} - z^6\mathrm{F}^\circ$ of Mn I. The resulting values of this calculation are given in table 15. A comparison that we have made of the observed intensities with the values given in table 15 shows that in all cases the intensity perturbations are in the right direction

and of the right order of magnitude to account for the observed asymmetries. We do not intend to give here our own intensities, because they have little quantitative value, representing only visual estimates. However, it must be noted that particular care was taken in these estimates, to note in each pair of two symmetrical unperturbed components which was the stronger when perturbed. Readers of this paper may check for themselves the accuracy of these results by making visual estimates of the component intensities in figure 4 and comparing their resulting values with those given near the components, which represent the calculated perturbed strengths.

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13. References

- M. Martinez-Risco, Anal. Soc. Esp. de Fis. y Quim. 9, 263 (1912); and Phys. Z. 13, 137 (1912).
 E. Back und A. Landé, Zeemaneffekt und Multiplett-struktur der Spektrallinien (Julius Springer, Berlin, 1022) 1925).
- [3] E. Back, Z. Phys. 13, 205, 1923.
 [4] G. R. Harrison and J. R. McNally, Jr., Phys Rev. 58, 708 (1940); J. P. Molnar and W. J. Hitchcock, J. Opt. Soc. Am. 30, 534 (1940); O. Laporte and J. E. Mack, Phys. Rev. 63, 257 (1942).
 [5] J. R. McNally, Jr. and G. R. Harrison, J. Opt. Soc. Am. 35, 584 (1945).
 [6] M. A. Catalán and Olga García-Riquelmo, uppublished.
- [6] M. A. Catalán and Olga García-Riquelme, unpublished material.
- Kiess and G. Shortley, J. Research NBS 42, 183 (1949) RP 1961.
- [8] M. A. Catalán and R. Velasco, Proc. Phys. Soc. [A] 63,
- 917 (1950). [9] M. A. Catalán and R. Velasco, J. Opt. Soc. Am. **40**, 653 (1950); Anal. Soc. Esp. de Fis. y Quim., A, **47**, 7
- [10] H. N. Russell, Proc. Nat. Acad. Sci. 11, 322 (1925).

Washington, July 9, 1951.