

MULTIPLY SEPARATIONS IN COMPLEX SPECTRA— PART II

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ABSTRACT. Expressions, derived by Goudsmit and Humphreys for multiplet separations in complex spectra, have been applied to the observed multiplets of d^3s and d^3p configurations in Zr I, Cb II, and Ti I, V II and Cr III. A comparison between the theoretical and the experimental values of the separation factors indicated agreement in the deeper terms and chiefly of the d^3s configuration. The method is expected to give only the order of magnitude of the separations when it is used for the purpose of predicting unknown structures.

INTRODUCTION

In a previous paper, by the authors (Rao and Rao, 1948) expressions for multiplet separations derived by Goudsmit (1928) for complex spectra due to equivalent electron configurations have been applied to certain spectra of vanadium, columbium, etc., which have been recently analysed extensively from a study of Zeeman effect and hyperfine structures of a large number of lines. The comparison indicated good agreement for the deeper terms; the spectrum of columbium II showed exceptionally large deviations. A similar comparison is attempted in this paper for the multiplet separations of terms arising from the general configurations such as d^3s and d^3p . For such configurations Goudsmit and Humphreys (1928) have derived formulæ for the separations of normal multiplets on the fundamental assumptions that they are due to the interaction energy between spin and orbital magnetism of the electrons. The interaction energy is expressible in the form,

$$\Gamma = A l s \cos (l s) \quad \dots (1)$$

in which

$$A = \sum_i a_i \frac{l_i}{l} \cos (l_i l) \frac{s_i}{s} \cos (s_i s)$$

The method of deriving the factor A in the case where we have a number of equivalent electrons was shown by Goudsmit, and referred to in the previous paper. For other configurations, Goudsmit and Humphreys (*loc. cit.*) have shown, that the interaction energy may be found in the terms of that of the equivalent group and the interaction energy of the added electron, provided the quantum vectors of the initial configuration remain unchanged.

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They have shown that, if the co-efficients A' and a_2 refer to the original multiplet and the added electron the factor A of the resultant term may be written as,

$$A = A' \left(\frac{l'}{l} \right) \cos(l'l) \frac{s'}{s} \cos(s's) + a_2 \frac{l_2}{l} \cos(l_2l) \frac{s_2}{s} \cos(s_2s)$$

where s is the resultant of the vectors s' and s_2 . Hence by substitution for the cosines it was derived that

$$A = A' \frac{s(s+1) + s'(s+1) - s_2(s_2+1)}{2s(s+1)} \times \frac{l(l+1) + l'(l'+1) - l_2(l_2+1)}{2l(l+1)} \\ + a_2 \frac{s(s+1) + s_2(s_2+1) - s'(s'+1)}{2s(s+1)} \times \frac{l(l+1) + l_2(l_2+1) - l'(l'+1)}{2l(l+1)} \quad \dots (2)$$

The application of this formula was illustrated by Goudsmit and Humphreys for the spectra of Fe and of ionised oxygen; agreement was found in A' values obtained from different multiplets. They expected this method to be useful in checking up the assignment of configurations and terms in complicated cases; it should also be useful in predicting the magnitude of level separations, where they are not known.

RESULTS AND DISCUSSION

In the following section results are shown of a check-up, attempted in the iso-electronic spectra of Zr I and Cb II and of Ti I, V II and Cr III, for which the spectral data are known extensively. All the data are collected in Tables I and II below. The first column gives the spectrum and the configuration. The second contains the spectral term or terms due to the configuration and also the theoretical values of the separation factor calculated from the expression (2) by substituting the appropriate l and s values for the ion and of the added electron; these latter values are indicated in the first column.

The observed spectral data are utilised in the following manner. Taking the example of Ti I (Table II) for each of the quintets and triplets due to the different configurations, the separation factor A is calculated (*i*) from adjacent levels using the general relation

$$\Gamma(j-1) - \Gamma(j) = A_j \quad \dots (3)$$

and (*ii*) from the total separation, by dividing this total by the sum of all j values except the lowest. The mean of all these values of A is shown in column (5). A' is then calculated from this mean, by the help of the expressions in column (2) and shown in column (6). For the ion too the same procedure is applied by taking the mean value of the separation factor obtained both from adjacent levels and the total separation; these are presented in the

last three columns. If agreement is perfect between theory and observation, the values of A' from the various terms should be constant and identical with that derived from the ion data.

TABLE I
Separations in Zr I and Cb II

Electron configuration.	Equation (2)	Separation factor A calculated from			A' calculated from A	A' calculated from the ion data.		
		Adjacent levels	Total separation	Mean value		Adjacent levels	Total separation	Mean value
Zr II d^3	${}^4F A = \Lambda$					101.8 101.3 101.1	112.9	107.1
Zr I d^3								
$l = 3 \quad s' = 1\frac{1}{2} \quad {}^1F + s$	${}^5F A = \frac{3}{4} A'$	69.7, 72.9, 75.2, 76.1	72.7	73.4	97.9			
$l_2 = 0 \quad s_2 = \frac{1}{2}$	${}^3F A = \frac{5}{4} A'$	90.5, 105.2	100.2	100.6	80.4			
d^3p								
$l' = 3 \quad s' = 1\frac{1}{2} \quad {}^4F + p$	${}^5G A = \frac{9}{16} A' + \frac{a_2}{16}$	74.9, 84.6, 92.7, 113.7	88.2	90.8				
$l_2 = 1 \quad s_2 = \frac{1}{2}$	${}^3G A = \frac{15}{16} A' - \frac{a_2}{86}$	81.4, 70.4	78.2	77.7				
	${}^5F A = \frac{11}{16} A' + \frac{a_2}{48}$	82.5, 70.2, 74.3, 74.1	77.8	77.0				
	${}^3F A = \frac{55A'}{48} - \frac{a_2}{48}$	Partial Inversion	58.4	58.4				
	${}^5D A = A' - \frac{a_2}{12}$	74.3, 79.9, 85.2, 89.1	79.6	81.6				
	${}^3D A = \frac{5A'}{3} + \frac{a_2}{12}$	120.1, 129.8	115.9	115.3				
	G terms $\Sigma A = \frac{3A'}{2}$			168.5	112.5			
	F .. $\Sigma A = \frac{11A'}{6}$			135.4	73.8			
	D .. $\Sigma A = \frac{8A'}{3}$			196.9	73.1			
	All quintets $\Sigma A = \frac{9A'}{4}$			249.6	110.7			
	All triplets $\Sigma A = \frac{15A'}{4}$			251.4	67.0			
	Total $\Sigma A = 6A'$			501.0	83.5			

TABLE I (contd.)

Electron configuration	Equation (2)	Separation factor A calculated from			A' calculated from A	A' calculated from the ion data		
		Adjacent levels	Total separation	Mean value		Adjacent levels	Total separation	Mean value
Cb III d^3	${}^4F \Lambda = A'$					169.5 188.5 206.8	184.7	187.4
Cb II d^3s								
d^3p	5F	120.7, 128.2	127.8	129.2	172.3			
	3F	133.5, 136.2 104.9, 131.6	116.3	117.6	94.1			
	5G	163.5, 168.4 178.2, 189.4	172.4	174.4				
	3G	153.6, 162.6	157.6	157.9				
	5F	99.2, 37.9, 138.1, 115.5	92.3	96.6				
	3F	195.2, 265.1	225.2	228.6				
	5D		99.3	99.3				
	3D	344.1, 317.3	333.4	331.6				
	G terms			332.4	221.6			
	F terms			325.2	177.4			
	D terms			430.9	161.6			
	Quintets			370.3	164.6			
	Triplets			718.1	191.5			
Total			1088	181.4				

The separation factors from adjacent levels are given in the tables in order to examine, at once, how far Lande's interval rule is obeyed and hence the conformity of the atom to the normal R-S coupling. Where adjacent levels happen to be irregular, values from the total separation alone are shown.

A check is possible for each term of the d^3s configuration; for the terms of the d^3p state, only the interval sums such as "of all the G terms" or "of all the quintets", etc., could be used to estimate A' , as the terms containing a_2 (which is not calculable) would then vanish.

Examination of the tables indicate a fairly close agreement in the spectra of titanium and an approximate one for chromium; the departures are large in the other spectra dealt with, *i.e.*, vanadium and columbium. In general, agreement is better for the deeper terms and terms of the d^3s configuration

TABLE II

Separations in Ti I, V II and Cr III

Electron configuration	Equation (2)	Separation factor Λ calculated from			Λ' calculated from Λ	Λ' calculated from the ion data		
		Adjacent levels	Total separation	Mean value		Adjacent levels	Total separation	Mean value
Ti II d^3	$4F \Lambda = \Lambda'$					28.5, 29.5, 30.3	29.3	29.4
Ti I $d^3 s$	$5F$	20.0, 20.4, 20.6, 20.5;	20.4	20.5	27.3			
$d^3 p$	$3F$	34.3, 36.0	35.0	35.1	28.1			
	$5G$	22.9, 23.1, 23.2, 23.3;	23.1	23.1				
	$3G$	27.1, 28.9	28.0	28.0				
	$5F$	21.5, 21.4, 21.3, 21.2,	21.4	21.3				
	$3F$	33.1, 30.1	31.7	31.6				
	$5D$	18.5, 26.3, 26.0, 26.1;	23.1	24.0				
	$3D$	47.9, 53.7	50.2	50.6				
	G terms			51.2	34.1			
	F terms			53.0	28.9			
	D terms			74.6	28.0			
Quintets			68.6	30.5				
Triplets			110.2	29.4				
Total			178.8	29.8				
VIII d^3	$4F \Lambda = \Lambda'$					54, 56, 58	56	56
VII $d^3 s$	$5F$	38.9, 39.9, 40.5, 41.1	39.8	40.1	53.5			
$d^3 p$	$3F$	63.9, 67.2	65.3	65.5	52.4			
	$5G$	48.4, 49.3, 50.2, 51.0,	49.5	49.7				
	$3G$	41.8, 42.4	42.1	42.1				
	$5F$	40.4, 57.8, 81.9, 92.1	61.6	66.8				
	$3F$	58.7, 64.6	61.2	61.5				
	$5D$		33.0	33.0				
	$3D$	54.6, 43.3	50.1	49.3				
G terms			91.8	61.2				
F terms			128.3	69.6				
D terms			82.3	30.8				
Quintets			149.5	66.4				
Triplets			152.9	40.8				
Total			302.4	50.4				
IV $d^3 s$	$4F \Lambda = \Lambda'$					88, 90, 3, 95	90.3	90.9
$d^3 p$	$5F$	64, 66, 67, 68	65	66	88			
	$3F$	108, 114	110	111	89			
	$5G$	84, 85, 87, 88	86	86				
	$3G$	65, 65,	65	65				
	$5G$	52, 60, 67, 74	60	62				
	$3F$	88, 101	94	95				
	$5D$	96, 109, 117	105	107				
	$3D$	126, 114	121	120				
	G terms			151	101			
	F terms			157	85			
D terms			227	102				
Quintets			255	113				
Triplets			280	75				
Total			535	89				

than for the others. The extent of the disagreement will indicate the measure of deviation from the Russel-Saunders type of coupling which is fundamentally assumed to be occurring in the atom, as is evident from equation (2).

As a method for the purpose of predicting the unknown structure of a spectrum, it may give us merely the order of magnitude of the separations and their approximate values, chiefly in terms of the d^3s configuration. It is hoped that guidance of this type would be of help in analysing complex spectra, in which Zeeman effect or other studies are difficult to carry out experimentally.

The data quoted in Tables I and II are taken from the references mentioned below.

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