MULTIPLET SEPARATIONS IN COMPLEX SPECTRA
PART III

(EQUIVALENT *f* ELECTRON CONFIGURATIONS)

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ABSTRACT. The separation factors have been calculated for multiplet-terms arising out of equivalent electron configurations of the type f^1 and f^2.

INTRODUCTION

In two previous papers the authors (Rao and Rao, 1948) discussed the applicability to certain known complex spectra of Goudsmit's expressions for mutliplet separations arising from electron configurations of the type d^3, d^4, d^3s and d^3p etc., and it was shown that the expressions could be used to a certain extent to the prediction of the intervals of the deeper set of terms in a spectrum. Goudsmit (1928) made the calculation of the separation factors only in the case of p^n and d^n electron systems, the latter forming the basic configurations for elements like vanadium, and chromium. The rare earth elements involve '*f*' type electron-configuration and it would be of interest to derive the expressions for these as well, as they might suggest at least approximate estimates of the magnitudes of the intervals in such spectra, which as yet are not analysed sufficiently.

CALCULATION OF THE SEPARATION FACTORS

The method of deriving the expressions for '*f*' electrons is as follows:—

(*a*) *Systems having one f election,* (f^1) :—For a single '*f*' electron $l=3$, $m_l=\pm 3, \pm 2, \pm 1, 0$ and $m_s=\pm\frac{1}{2}$.

Writing down the possible combinations (14 in all) we have :

TABLE I

m_s	m_l	r/a	M	m_s	m_l	r/a	M
$\frac{1}{2}$	3	3/2	$3\frac{1}{2}$	$-\frac{1}{2}$	3	$-3/2$	$2\frac{1}{2}$
	2	1	$2\frac{1}{2}$		2	-1	$1\frac{1}{2}$
	1	$\frac{1}{2}$	$1\frac{1}{2}$		1	$-\frac{1}{2}$	$\frac{1}{2}$
	0	0	$\frac{1}{2}$		0	0	$-\frac{1}{2}$
	-1	$-\frac{1}{2}$	$-\frac{1}{2}$		-1	$\frac{1}{2}$	$-1\frac{1}{2}$
	-2	-1	$-1\frac{1}{2}$		-2	1	$-2\frac{1}{2}$
	-3	$-3/2$	$-2\frac{1}{2}$		-3	3/2	$-3\frac{1}{2}$

The second column contains $m_s m_l = \tau/a$. In the third column are given $m_s + m_l = \mathrm{M}$. Another table is drawn from the above as follows:

TABLE II

M_s \ M	$3\frac{1}{2}$	$2\frac{1}{2}$	$1\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-1\frac{1}{2}$	$-2\frac{1}{2}$	$-3\frac{1}{2}$
$\frac{1}{2}$	$3/2$	1	$\frac{1}{2}$	0	$-\frac{1}{2}$	-1	$-3/2$	
$-\frac{1}{2}$		$-3/2$	-1	$-\frac{1}{2}$	0	$\frac{1}{2}$	1	$3/2$
$\Sigma\tau$	$3/2$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$3/2$

which gives the τ sums in a weak field. A similar table is prepared in the case of a strong field as follows: the terms arising out of a single '*f*' electron are ${}^2\mathrm{F}_{3\frac{1}{2}}$ and ${}^2\mathrm{F}_{2\frac{1}{2}}$. If we put ${}^2\mathrm{F}_{3\frac{1}{2}} = \tau_1$ and ${}^2\mathrm{F}_{2\frac{1}{2}} = \tau_2$, τ_1 and τ_2 being their separations from a hypothetical level, we have in a strong field :

TABLE III

J \ M	$3\frac{1}{2}$	$2\frac{1}{2}$	$1\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-1\frac{1}{2}$	$-2\frac{1}{2}$	$-3\frac{1}{2}$
$3\frac{1}{2}$	τ_1	τ_1	τ_1	τ_1	τ_1	τ_1	τ_1	τ_1
$2\frac{1}{2}$		τ_2	τ_2	τ_2	τ_2	τ_2	τ_2	
$\Sigma\tau$	τ_1	$\tau_2+\tau_1$	$\tau_2+\tau_1$	$\tau_2+\tau_1$	$\tau_2+\tau_1$	$\tau_2+\tau_1$	$\tau_2+\tau_1$	τ_1

It is easy to see the symmetrical disposition of the $\Sigma\tau$ values about a centre. Equating the corresponding $\Sigma\tau$ values *i.e.*, belonging to the same M we have :

$$\tau_1 = 3/2 \text{ and } \tau_1 + \tau_2 = -\tfrac{1}{2}$$

$$\therefore \quad \tau_2 = -2 \text{ and } \tau_1 - \tau_2 = \tfrac{7}{2}$$

$\tau_1 - \tau_2$ gives the total separation in the ${}^2\mathrm{F}$ multiplet and is equal to $7/2\ a$.

Applying the Lande interval rule and dividing the separation by the higher of the J-values, we have the separation factor

$$\mathrm{A} = (7/2)a. \ \ (2/7) = a\,;$$

thus for a ${}^2\mathrm{F}$ in an '*f*' configuration we have the total separation $= 7/2\ a$ and the separation factor $\mathrm{A} = a$.

(*b*) "f^2" *configuration*:—In case of the two '*f*' electrons the broad principles mentioned above hold and certain new features set in. As before we write down the m_s, m_l values for each electron as follows :

TABLE IV

m_{s_1}	m_{l_1}	m_{s_2}	m_{l_1}	M_S	M_L	M	τ_1/a	τ_2/a	τ/a
$\frac{1}{2}$	3	$\frac{1}{2}$	3(x)	1	6	7	3/2	3/2	3
			2		5	6		1	$2\frac{1}{2}$
			1		4	5		$\frac{1}{2}$	2
			0		3	4		0	$1\frac{1}{2}$
			-1		2	3		$-\frac{1}{2}$	1
			-2		1	2		-1	$\frac{1}{2}$
			-3		0	1		$-1\frac{1}{2}$	0
		$-\frac{1}{2}$	3	0	6	6		$-1\frac{1}{2}$	0
			2		5	5		-1	$\frac{1}{2}$
			1		4	4		$-\frac{1}{2}$	1
			0		3	3		0	$1\frac{1}{2}$
			-1		2	2		$\frac{1}{2}$	2
			-2		1	1		1	$2\frac{1}{2}$
			-3		0	0		$1\frac{1}{2}$	3

Table IV is only a typical portion of an extensive table, setting out all the possible combinations. For each of one type of m_{s_1}, m_{l_1} combination, m_{s_2}, m_{l_2} can have 14 combinations. Among these, however, the combination marked (x) is not allowed by Pauli's exclusion principle, because n, l being the same for the eqvivalent electrons the m_s, m_l values cannot be both identical. Thus writing for different m_l, $3, 2, 1, 0, -1, -2, -3$, and also for the negative values of m_{s_1} *i.e.* $-\frac{1}{2}$, we will have 14×13 combinations. Of these there will be many combinations which are obtained by mere exchange of places, as in $\frac{1}{2}$ 2, $\frac{1}{2}$ 3; $\frac{1}{2}$ 3, $\frac{1}{2}$ 2, which are not different configurations. In fact we get each combination 2 times. Therefore the net permissible combinations are $\frac{1}{2}(14 \times 13) = 91$. The 13 combinations in the above table are among the permissible ones. Column (2) in Table IV contains

$$M_S = m_{s_1} + m_{s_2},\ M_L = m_{l_1} + m_{l_2},\ \text{and } M = M_S + M_L.$$

and column (3) gives,

$$\frac{\tau_1}{a} = m_{s_1} m_{l_1}\ ;\ \frac{\tau_2}{a} = m_{s_2} . m_{l_2}$$

and

$$\frac{\tau}{a} = \frac{\tau_1}{a} + \frac{\tau_2}{a}$$

From such a complete table, we form another, similar to Table II, giving sums in strong field. The net result is given below in Table V.

TABLE V

M_s \ M	6	5	4	3	2	1	0	−1	−2	−3	−4	−5	−6
1	5/2	2	3	2	3/2	0	−3/2	−2	−3	−2	−5/2		
0	0	0	0	0	0	0	0	0	0	0	0	0	0
−1			−5/2	−2	−3	−2	−3/2	0	3/2	2	3	2	5/2
$\Sigma\tau$	5/2	2	1/2	0	−3/2	−2	−3	−2	−3/2	0	1/2	2	5/2

TABLE VI

M	6	5	4	3	2	1	0	−1	−2	−3	−4	−5	−6
$^3F_4$			$3A_F$	$3A_F$	$3A_F$	$3A_F$	$3A_F$	$3A_F$	$3A_F$	$3A_F$	$3A_F$		
$^3F_3$				$-A_F$	$-A_F$	$-A_F$	$-A_F$	$-A_F$	$-A_F$	$-A_F$			
$^3F_2$					$-4A_F$	$-4A_F$	$-4A_F$	$-4A_F$	$-4A_F$				
$^3P_2$					A_P	A_P	A_P	A_P	A_P				
$^3P_1$						$-A_P$	$-A_P$	$-A_P$					
$^3P_0$							$-A_P$						
$^3H_6$	$5A_H$	$5A_H$	$5A_H$	$5A_H$	$5A_H$	$5A_H$	$5A_H$	$5A_H$	$5A_H$	$5A_H$	$5A_H$	$5A_H$	$5A_H$
$^3H_5$		$-A_H$	$-A_H$	$-A_H$	$-A_H$	$-A_H$	$-A_H$	$-A_H$	$-A_H$	$-A_H$	$-A_H$	$-A_H$	
$^3H_4$			$-6A_H$	$-6A_H$	$-6A_H$	$-6A_H$	$-6A_H$	$-6A_H$	$-6A_H$	$-6A_H$	$-6A_H$		
$\Sigma\tau$	$5A_H$	$4A_H$	$3A_F-2A_H$	$2A_F-2A_H$	$-2A_F+A_P-2A_H$	$-2A_F-2A_H$	$-2A_F-2A_P-2A_H$	$-2A_F-2A_H$	$-2A_F+A_P-2A_H$	$2A_F-2A_H$	$3A_F-2A_H$	$4A_H$	$5A_H$

Taking by corresponding M's we have,

$$5A_H=\tfrac{5}{2}a \quad \text{or} \quad A_H=\tfrac{1}{2}a$$

$$3A_F-2A_H=\tfrac{1}{2}a \quad \text{or} \quad A_F=\tfrac{1}{2}a \text{ and}$$

$$-2A_F-2A_H+A_P=-\tfrac{3}{2}a \quad \text{or} \quad A_P=\tfrac{1}{2}a$$

$$i.e.\ A_H=A_F=A_P=\tfrac{1}{2}a$$

Preparing the $\Sigma\tau$ table for strong field we have for different J values of different multiplets different τ's over a bypothetical level and they will be of the general form as in the case of "f^1" configuration (of the type of $\Sigma\tau_1$ etc.,). Taking these, as before, under corresponding M values and equating, we see that there are more constants to be determined than the available equations. To get over this mathematical difficulty the following simplification is made on the assumption that the Lande-interval rule strictly holds. Illustratively, in the case of $^3P_{2,1,0}$ we have by Lande-interval rule $^3P_2 - {}^3P_1 = 2A_P$ and $^3P_1 - {}^3P_0 = A_P$, where A_P is the separation factor and the separation is proportional to the higher J value. If we put $^3P_2$ as having a value A_P and $^3P_1$ a value $-A_P$ then $^3P_2 - {}^3P_1 = 2A_P$ proportional to 2 and $^3P_0$ a value $-2A_P$ then $^3P_1 - {}^3P_0 = A_P$ which is again proportional to l. Thus suitably choosing numerical coefficients, we can easily see that there is only one constant A_P to be determined. Thus we can suitably arrange to get only one constant for each multiplet-term and solve the equation easily. It would not be difficult to see that the question of separations does not arise in case of singlets as they are single levels and so we can treat them as zero.

RESULTS

From the above, the total separations for ^3F, ^3P and ^3H are follows :—

$$^3F = 7/2a \qquad ^3P = 3/2a \quad . \; ^3H = 11/2a$$

The separation factor for each multiplet is $\frac{1}{2}a$.

The same method may be adopted for the calculation of the factors for f^3, f^4 etc., configurations, only, the table of permissible combinations would be much more extensive.

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