

Only one configuration remains  $M_L=0$ ,  $M_S=0$  which can give only a  $^1S$  term ( $L=0$ ,  $S=0$ ).

$$\left. \begin{array}{l} M_L = 0 \\ M_S = 0 \end{array} \right\} ^1S.$$

Thus two equivalent  $p$ -electrons give rise to  $^1D$ ,  $^3P$  and  $^1S$  terms; and no others. The fine-structure levels are  $^1D_2$ ,  $^3P_{0,1,2}$  and  $^1S_0$ .

The same terms are readily calculated from Breit's scheme. In this scheme we write in a table all the possible values of  $M_L$  which can be formed by the combination of  $m_{l_1}$  and  $m_{l_2}$  of the two electrons. For this we write the values of  $m_{l_1}$  and  $m_{l_2}$  in a row and column respectively. The sums  $M_L$  are written below  $m_{l_1}$  and to the left of  $m_{l_2}$ . These nine values of  $M_L$  form three sets divided by the L-shaped (dotted) lines. These sets are:

$m_{l_1} =$	1	0	-1	
$M_L =$	2	1	0	1
$M_L =$	1	0	-1	0
$M_L =$	0	-1	-2	-1
		S	P	D
				$m_{l_2}$

(two equivalent  $p$ -electrons)  
 $l_1=1$ ;  $l_2=1$

- 2 1 0 -1 -2 (I set)  
1 0 -1 (II set)  
0 (III set)

These sets of  $M_L$ -values correspond to  $L=2$ , 1 and 0 respectively i.e. to one  $D$ , one  $P$ , and one  $S$  term.

The spins of the two electrons can be combined to form either  $S=0$  (singlets) or  $S=1$  (triplets). For  $S=1$ , both electrons have the same spin quantum number  $m_s$  and hence they must differ in their values of  $m_l$ . We cannot, therefore, combine any of the  $M_L$ -values lying on the diagonal of the above table with  $S=1$  (because the diagonal corresponds to equal values of  $m_{l_1}$  and  $m_{l_2}$ ). Also, we can use only the  $M_L$ -values from one side of the diagonal, as those on the other side merely correspond to a different numbering of the electrons (otherwise they are identical with, and are a mirror image of those on the first side). Thus, with  $S=1$  (triplets), we are limited to the following  $M_L$ -values.

$$1, 0, -1 \text{ (II set)}$$

which are the components of a term with  $L=1$ . This corresponds to a  $^3P$  term or a  $^3P_{0,1,2}$  multiplet.

When  $S=0$ , the electrons differ in their spin quantum numbers and there is no restriction on the values of  $M_L$  which may be combined with this value of  $S$ . As the II set of  $M_L$  values has already been used to form the  $^3P$  term, we have only the remaining I and III sets to combine with  $S=0$  (singlets). These sets are the components of terms with  $L=2$  and  $L=0$  respectively. Hence they correspond to  $^1D$  and  $^1S$  terms.



Thus two equivalent  $p$ -electrons give  $^1S$ ,  $^1D$  and  $^3P$  terms or  $^1S_0$ ,  $^1D_2$  and  $^3P_{0,1,2}$  multiplets.

These will also be the terms for  $p^4$  configuration.

Let us now consider two equivalent  $d$ -electrons i.e.  $(nd)^2$  configuration. The Breit's scheme for the possible  $M_L$ -values is :

$m_{l_1} =$	2	1	0	-1	-2	
$M_L =$	4	3	2	1	0	2
$M_L =$	3	2	1	0	-1	1
$M_L =$	2	1	0	-1	-2	0
$M_L =$	1	0	-1	-2	-3	-1
$M_L =$	0	-1	-2	-3	-4	-2
	S	P	D	F	G	$m_{l_2}$

(two equivalent  $d$ -electrons)

$$l_1=2; l_2=2.$$

There are 5 sets of  $M_L$ -values :

4	3	2	1	0	-1	-2	-3	-4	(I set)
	3	2	1	0	-1	-2	-3		(II set)
		2	1	0	-1	-2			(III set)
			1	0	-1				(IV set)
				0					(V set)

These sets correspond to  $L=4, 3, 2, 1, 0$  respectively i.e. to  $G, F, D, P, S$  terms respectively.

The spins of the two electrons can be combined to form either  $S=0$  (singlets) or  $S=1$  (triplets). For  $S=1$ , we are limited to the  $M_L$  values from one side of the diagonal i.e. to the following sets :

3	2	1	0	-1	-2	-3	(II set)
		1	0	-1			(IV set)

These sets correspond to  $L=3$  and  $L=1$  and give  $^3F$  and  $^3P$  terms or  $^3F_{2,3,4}$  and  $^3P_{0,1,2}$  multiplets.

The remaining I, III, and V set of  $M_L$ -values are to be combined with  $S=0$  (singlets). They yield  $^1G$ ,  $^1D$  and  $^1S$  terms. Thus two equivalent  $d$ -electrons give

$$^1S_0, ^1D_2, ^1G_4, ^3P_{0,1,2}, ^3F_{2,3,4}.$$

These will also be the terms for  $d^8$  configuration.

As a final example, we now calculate the spectral terms arising from  $p^3$  configuration. The six possible states for a single  $p$ -electron in a very strong field are



$$\begin{aligned}
 m_l &= 1 \quad 0 \quad -1 \quad 1 \quad 0 \quad -1 \\
 m_s &= \frac{1}{2} \quad \frac{1}{2} \quad \frac{1}{2} \quad -\frac{1}{2} \quad -\frac{1}{2} \quad -\frac{1}{2} \\
 &\quad (a) \quad (b) \quad (c) \quad (d) \quad (e) \quad (f)
 \end{aligned}$$

The possible states for three (equivalent) electrons can be obtained by taking all possible combinations of the above six states taken three at a time, with no two alike. There will be 20 such

combinations  $\left( {}^6C_3 = \frac{6!}{3!(6-3)!} = 20 \right)$ . They are

$$\begin{aligned}
 &abc \quad abd \quad abe \quad abf \quad acd \quad ace \quad acf \quad ade \quad adf \quad aef \\
 &bcd \quad bce \quad bcf \quad bde \quad bdf \quad bef \quad cde \quad cdf \quad cef \quad def
 \end{aligned}$$

For each of these 20 combinations we obtain  $M_L (= \Sigma m_l)$  and  $M_S (= \Sigma m_s)$ . This leads to the following tabulation :

	<i>abc</i>	<i>abd*</i>	<i>abe*</i>	<i>abf*</i>	<i>acd**</i>	<i>ace**</i>	<i>acf*</i>	<i>ade*</i>	<i>adf*</i>	<i>aef*</i>
$M_L = 0$	2	1	0	1	0	-1	2	1	0	
$M_S = \frac{3}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
	<i>bcd</i>	<i>bce**</i>	<i>bcf*</i>	<i>bde**</i>	<i>bdf**</i>	<i>bef*</i>	<i>cde</i>	<i>cdf**</i>	<i>cef*</i>	<i>def</i>
$M_L = 0$	-1	-2	1	0	-1	0	-1	-2	0	
$M_S = \frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$

The highest values of  $M_L$  are 2 which indicate a  $D$ -term ( $L=2$ ). Since they occur with  $M_S = \frac{1}{2}$  and  $M_S = -\frac{1}{2}$ , which are the magnetic field components of  $S = \frac{1}{2}$ , the term is  ${}^3D$ . Apart from  $M_L = 2$ ;  $M_L = 1, 0, -1, -2$  and each with  $M_S = \frac{1}{2}$  and  $M_S = -\frac{1}{2}$  also belong to this term. Thus out of the above 20 combinations those marked as\* go to form the  ${}^2D$  term.

Of the remaining combinations, the highest  $M_L$  are 1, and again they occur with  $M_S = \frac{1}{2}$  and  $M_S = -\frac{1}{2}$ . They indicate, therefore, a  ${}^3P$  term ( $L=1, S=\frac{1}{2}$ ). Apart from  $M_L = 1$ ;  $M_L = 0, -1$  and each with  $M_S = \frac{1}{2}$  and  $M_S = -\frac{1}{2}$  also belong to this term. Hence the combinations marked\*\* belong to the  ${}^2P$  term.

The remaining four combinations are :

$$\begin{aligned}
 M_L &= 0 \quad 0 \quad 0 \quad 0 \\
 M_S &= \frac{3}{2} \quad \frac{1}{2} \quad -\frac{1}{2} \quad -\frac{3}{2}
 \end{aligned}$$

These  $M_L$  and  $M_S$  values are the components of  $L=0$  and  $S=\frac{3}{2}$  which correspond to a  ${}^4S$  term. Thus the terms of  $p^3$  are

$${}^3P^\circ, {}^2D^\circ, {}^4S^\circ$$

or

$${}^3P^\circ_{1/2, 3/2}; {}^2D^\circ_{3/2, 5/2}; {}^4S^\circ_{3/2}$$