

(3) **Atoms with Two or More Equivalent Electrons**—For two equivalent electrons (same  $n$  and  $l$  values) the values of at least one the remaining quantum numbers ( $m_l$  or  $m_s$ ) must differ to satisfy Pauli's exclusion principle. Hence certain terms which were possible for two non-equivalent electrons are now not allowed. For instance, two non-equivalent  $p$ -electrons, such as  $2p$  and  $3p$ , give rise to the terms  $^1S$ ,  $^1P$ ,  $^1D$ ,  $^3S$ ,  $^3P$ ,  $^3D$ ; but if the two electrons are equivalent, say  $2p^2$ , then the terms  $^3D$ ,  $^3S$  and  $^1P$  do not exist and we have only the terms  $^1S$ ,  $^1D$  and  $^3P$ . Let us now see how to obtain terms from a configuration involving

equivalent electrons. Before we do so we must mention two important facts :

(i) A closed sub-shell, such as  $s^2, p^6, d^{10}, \dots$  always forms a  $^1S_0$  term only. The closed sub-shell consists of maximum number,  $2(2l + 1)$ , of equivalent electrons in antiparallel pairs so that

$$\Sigma m_l = 0^*$$

$$\Sigma m_s = 0^*.$$

and

This means that

$$M_L = 0, M_S = 0$$

and so

$$L = 0 \text{ (S-State)}$$

$$S = 0, 2S + 1 = 1 \text{ (singlet)}$$

and

$$J = 0.$$

That is, the only possible term is  $^1S_0$ . Hence we conclude that when a subshell is completely filled, the only allowed state is one in which the total spin angular momentum, total orbital angular momentum and total angular momentum are all zero. This also means that the subshell has no net magnetic dipole moment.

(ii) The terms of a configuration  $(nl)^a$  are the same as the terms of the configuration  $(nl)^{r-a}$ , where  $r$  is the maximum number of electrons, that is  $2(2l + 1)$ . For example the terms of  $p^5$  are the same as those of  $p^1$ , the terms of  $p^4$  are the same as those of  $p^2$ , the terms of  $d^8$  are the same as those of  $d^2$ , and so on.

This simplification is based on the fact that a completed sub-shell like  $p^6$  gives only a  $^1S_0$  term (zero angular momenta). This means that the vector addition of the angular momenta of the terms of  $p^2$  (say) to the corresponding quantities for  $p^4$  must give zero. From this it follows that the quantum numbers  $S$  and  $L$  must be the same for  $p^2$  and  $p^4$  i.e. the terms of  $p^2$  are the same as those of  $p^4$ .

We now calculate the spectral terms arising from two equivalent  $p$ -electrons ( $p^2$ ). Let us imagine the atom to be placed in a very strong magnetic field where all the internal couplings are broken down. The individual  $\vec{l}$  and  $\vec{s}$  vectors then precess independently round the magnetic field with quantised components  $m_l h/2\pi$  and  $m_s h/2\pi$  respectively. The value of  $l$  for a  $p$ -electron is 1 and hence the values of  $m_l$  are 1, 0, -1 while those of  $m_s$  are  $+\frac{1}{2}$  and  $-\frac{1}{2}$ . Now, all possible combinations of  $m_l$  and  $m_s$  for a single  $p$ -electron are :

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

Thus there are six possible states (*a*), ..... (*f*) in which a single *p*-electron can exist in an atom. The possible states for two (equivalent) electrons can be obtained by taking all possible combinations of the above six states taken two at a time, with no two alike (because by Pauli's principle, both  $m_l$  and  $m_s$  cannot be same for the two electrons). There will be 15 such combinations

$$\left( {}^6C_2 = \frac{6!}{2!(6-2)!} = 15 \right). \text{ They are}$$

*ab, ac, ad, ae, af;*  
*bc, bd, be, bf;*  
*cd, ce, cf;*  
*de, df;*  
*ef.*

For each of these 15 combinations of very strong field quantum numbers we add the two values of  $m_l$  to obtain the strong field values of  $M_L$ , and the two values of  $m_s$  to form  $M_S$  [ $\sum m_l = M_L$  and  $\sum m_s = M_S$ ]. This leads to the following tabulation :

	<i>ab</i>	<i>ac</i>	<i>ad</i>	<i>ae</i>	<i>af</i>	<i>bc</i>	<i>bd</i>	<i>be</i>	<i>bf</i>	<i>cd</i>	<i>ce</i>	<i>cf</i>	<i>de</i>	<i>df</i>	<i>ef</i>
$M_L$	1	0	2	1	0	-1	1	0	-1	0	-1	-2	1	0	-1
$M_S$	1	1	0	0	0	1	0	0	0	0	0	0	-1	-1	-1

The highest value of  $M_L$  is 2 which indicates a *D* term ( $L=2$ ). Since this value of  $M_L$  occurs only with  $M_S=0$ , the term is  ${}^1D$  ( $S=0$ ). Apart from  $M_L=2$ ;  $M_L=1, 0, -1, -2$  also belong to this term, each having  $M_S=0$ . Thus out of the above 15 combinations, the following form  ${}^1D$  term.

$$\left. \begin{array}{l} M_L = 2 \quad 1 \quad 0 \quad -1 \quad -2 \\ M_S = 0 \quad 0 \quad 0 \quad 0 \quad 0 \end{array} \right\} {}^1D.$$

Of the remaining  $M_L$  and  $M_S$  values, the highest  $M_L$  is 1 and the highest  $M_S$  is 1. These values must belong to a  ${}^3P$  term ( $L=1, S=1$ ), because only for such a term can the highest values of  $M_L$  and  $M_S$  be 1. But  $L=1$  corresponds to  $M_L = 1, 0, -1$ ; and  $S=1$  corresponds to  $M_S = 1, 0, -1$ . Hence all the following nine configurations belong to the  ${}^3P$  term :

$$\left. \begin{array}{l} M_L = 1 \quad 0 \quad -1 \quad 1 \quad 0 \quad -1 \quad 1 \quad 0 \quad -1 \\ M_S = 1 \quad 1 \quad 1 \quad 0 \quad 0 \quad 0 \quad -1 \quad -1 \quad -1 \end{array} \right\} {}^3P.$$