CHAPTER 8

Electronic Spectra of Transition Metal Complexes:

❖ Spectroscopic Ground States

The spectra of transition metal complexes is not as simple as it appears from just the splitting of *d*-orbitals with electrons get promoted from the lower energy orbital set to a higher energy orbital set. Actually, energy levels of a transition metal atom or ion with a particular electronic configuration are described not only by the electronic configuration itself but also by different types of electronic interactions such as spin-spin, orbital-orbital or spin-orbital which can be categorized by some special symbols, called as term symbols. The ground state term symbol is predicted by Hund's rule. In other words, the term symbol in quantum mechanics is an abbreviated description of the total angular momentum quantum numbers in a multi-electron atom. However, the quantum mechanical states of a single electron can also be described by a term symbol.

➢ *Calculation of Microstates in a Particular Electronic Configuration*

The various overall-arrangements of electronic cloud around the nucleus for a particular configuration are not the same as far as the energy and angular momentum are concerned. These different electronic arrangements can be classified on the basis of overall spin, orbital or total angular momentum.

The term microstates may be defined as the overall electronic arrangements of a particular electronic configuration which can be differentiated in terms of energy or angular momentum.

The two types of electronic configurations for which the microstate calculation has to be carried out are discussed below.

1. When unpaired electrons are present in the same subshell:

i) p^1-configuration: Let us consider that we want to study the number of ways in which a single electron can be filled in any *p*-subshell.

	p_x	p_y	p_z
1	↑		
2	↓		
3		↑	
4		↓	
5			↑
6			↓

ii) p^2-configuration: Let us consider that we want to study the number of ways in which two electrons can be filled in any p-subshell.

	p_x	p_y	p_z
1	↑	↑	
2		↑	↑
3	↑		↑
4	↓	↓	
5		↓	↑
6	↓		↓
7	↑	↓	
8	↑		↓
9	↑		↓
10	↓	↑	
11		↓	↑
12		↓	↑
13	↑↓		
14		↑↓	
15			↑↓

Hence, the total number of ways in which one and two electrons can be arranged in the p-subshell of an atom or ion are six and fifteen, respectively. However, the calculation of the number of microstates for the configurations like d^2 or f^2 using the abovementioned method is quite lengthy and difficult. Moreover, as we are interested only in the number of these electronic arrangements and not in the nature; permutation and combination can be used to find out all these numbers as follows:

$$\text{No. of microstates} = \binom{n}{r} = \frac{n!}{r!\,(n-r)!}$$

Where n is twice the number of orbitals present in the subshell under consideration and r is the number of unpaired electrons in them. The formulation related to the calculation of the number of microstate in particular term symbol will be discussed later in this chapter.

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Now, the number of microstates for different electronic configurations can be calculated easily.

i) For p^1-configuration, $n = 6$ and $r = 1$. Therefore

$$\text{No. of microstates} = \binom{6}{1} = \frac{6!}{1!\,(6-1)!}$$

$$\binom{6}{1} = \frac{6 \times 5 \times 4 \times 3 \times 2 \times 1}{1(5 \times 4 \times 3 \times 2 \times 1)}$$

$$= 6 \text{ microstates}$$

ii) For p^2-configuration, $n = 6$ and $r = 2$. Therefore

$$\text{No. of microstates} = \binom{6}{2} = \frac{6!}{2!\,(6-2)!}$$

$$\binom{6}{2} = \frac{6 \times 5 \times 4 \times 3 \times 2 \times 1}{2 \times 1(4 \times 3 \times 2 \times 1)}$$

$$= 15 \text{ microstates}$$

iii) For d^1-configuration, $n = 10$ and $r = 1$. Therefore

$$\text{No. of microstates} = \binom{10}{1} = \frac{10!}{1!\,(10-1)!}$$

$$\binom{10}{1} = \frac{10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1}{1(9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1)}$$

$$= 10 \text{ microstates}$$

iv) For d^2-configuration, $n = 10$ and $r = 2$. Therefore

$$\text{No. of microstates} = \binom{10}{2} = \frac{10!}{2!\,(10-2)!}$$

$$\binom{10}{2} = \frac{10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1}{2 \times 1(8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1)}$$

$$= 45 \text{ microstates}$$

The general form of atomic term symbols considers spin-spin (S-S coupling), orbital-orbital (L-L coupling) and spin-orbital (L-S or Russell-Saunders coupling) interactions; therefore, before categorizing all the microstates in these term symbols, it is extremely important to find out all possible microstates for different electronic configurations. The total number of microstates for other different electronic configurations can be calculated using the same method and are listed below.

Table 1. The calculated microstates for different electronic configurations.

Electronic configuration	No. of microstates	Electronic configuration	No. of microstates
p^1	6	d^3	120
p^2	15	d^4	210
p^3	20	d^5	252
p^4	15	d^6	210
p^5	6	d^7	120
p^6	1	d^8	45
d^1	10	d^9	10
d^2	45	d^{10}	1

It can be seen that the number of microstates for the same number of unpaired electrons is equal. For example, there are six microstates for p^1 as well as p^5 and forty-five microstates for both d^2 as well as d^8. It can be explained in terms of electron-hole formalism which will be discussed later in this chapter.

2. When unpaired electrons are present in different subshell:

The same approach can also be applied to calculate the microstates in the case when the electrons are present in two different subshells. Therefore, permutation and combination can be used to find out all these numbers as follows:

$$\text{No. of microstates} = \left(\frac{n}{r}\right) \times \left(\frac{m}{s}\right) = \frac{n!}{r!\,(n-r)!} \times \frac{m!}{s!\,(m-s)!}$$

Where, n is twice the number of orbitals and r is the number of unpaired electrons in one subshell while m is twice the number of orbitals and s is the number of unpaired electrons in the other subshell. Now, the number of microstates for different electronic configurations can be calculated easily.

i) p^1p^1-configuration, $n = 6$, $r = 1$, $m = 6$ and $s = 1$.

$$\text{No. of microstates} = \left(\frac{6}{1}\right) \times \left(\frac{6}{1}\right) = \frac{6!}{1!\,(6-1)!} \times \frac{6!}{1!\,(6-1)!}$$

$$\left(\frac{6}{1}\right) \times \left(\frac{6}{1}\right) = \frac{6 \times 5 \times 4 \times 3 \times 2 \times 1}{1(5 \times 4 \times 3 \times 2 \times 1)} \times \frac{6 \times 5 \times 4 \times 3 \times 2 \times 1}{1(5 \times 4 \times 3 \times 2 \times 1)}$$

$$= 36 \text{ microstates}$$

ii) d^1d^1-configuration, $n = 10$, $r = 1$, $m = 10$ and $s = 1$.

$$\text{No. of microstates} = \left(\frac{10}{1}\right) \times \left(\frac{10}{1}\right) = \frac{10!}{1!\,(10-1)!} \times \frac{10!}{1!\,(10-1)!}$$

$$\left(\frac{10}{1}\right) \times \left(\frac{10}{1}\right) = \frac{10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1}{1(9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1)} \times \frac{10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1}{1(9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1)}$$

$$= 100 \text{ microstates}$$

iii) p^1d^1-configuration, $n = 6$, $r = 1$, $m = 10$ and $s = 1$.

$$\text{No. of microstates} = \left(\frac{6}{1}\right) \times \left(\frac{10}{1}\right) = \frac{6!}{1!\,(6-1)!} \times \frac{10!}{1!\,(10-1)!}$$

$$\left(\frac{6}{1}\right) \times \left(\frac{10}{1}\right) = \frac{6 \times 5 \times 4 \times 3 \times 2 \times 1}{1(5 \times 4 \times 3 \times 2 \times 1)} \times \frac{10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1}{1(9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1)}$$

$$= 60 \text{ microstates}$$

The total number of microstates for different electronic configurations can be calculated using the same method and are listed below.

Table 2. The total number of microstates calculated for the different electronic configurations when unpaired electrons are present in two different subshells.

Electronic configuration	No. of microstates	Electronic configuration	No. of microstates
p^1p^1	36	d^2d^2	2025
p^1p^2	90	d^2d^3	5400
p^2p^2	225	p^1d^1	60
p^2p^3	300	p^1d^2	270
d^1d^1	100	p^2d^2	675
d^1d^2	450	p^2d^3	1800

This table can further be extended for the remaining combination of *p-p*, *d-d*, *p-d* or their combinations with *f*-subshell. The number of microstates in particular configuration can be distributed to various electronic states, represented by atomic term symbols. The distribution of these microstates in different term symbols will be discussed later in this section.

> ➤ *Atomic Term Symbols*

Atomic term symbols may be defined as the symbolic representations of various electronic states having different resultant angular momentums resulting from spin-spin, orbital-orbital or spin-orbital interactions and the transitions between two different atomic states may also be represented using their term symbols, to which certain rules apply.

The general form of any atomic term symbol that is used to represent any electronic state resulting from inter-electronic repulsion is:

$$^{2S+1}L_J$$

Where,

2S+1 = spin multiplicity

S = resultant spin angular momentum quantum number

L = resultant orbital angular momentum quantum number

J = resultant total angular momentum quantum number

Just like in the case of atomic orbitals, where l represents the individual orbital angular momentums; L represents the resultants orbital angular momentum of an electronic state and gives the base designation of any atomic term symbol.

L	=	0	1	2	3	4	5	6	7
State	=	S	P	D	F	G	H	I	K

The calculation of resultant spin and orbital angular momentum involves the concepts of space quantization and vector interactions. A somewhat simplified approach for the calculation of resultant orbital angular momentum quantum number (L), resultant spin angular momentum quantum number S and resultant total angular momentum quantum number (J) can be given by understanding the spin-spin, orbital-orbital and spin-orbital couplings schemes.

1. Orbital-orbital coupling (*l-l* interaction): Consider a multielectron system, then the resultant orbital angular momentum quantum number can be deduced as:

$$L = (l_1 + l_2),\ (l_1 + l_2 - 1) \dots\dots |l_1 - l_2|$$

Where l_1 and l_2 are the individual orbital angular momentum quantum numbers for electrons and modulus sign shows that the value of resultant orbital angular momentum quantum number is always positive. Given the eigenstates of l_1 and l_2, the construction of eigenstates of L (which still is conserved) is the coupling of the angular momenta of electrons 1 and 2.

i) For p^1p^1-configuration, $l_1 = 1$ and $l_2 = 1$, therefore

$$L = (1 + 1), \ (1 + 1 - 1), \ (1 - 1)$$

$$L = 2, 1, 0$$

$$\text{States} = D, P, S$$

Similarly,

ii) For d^1d^1-configuration, $l_1 = 2$ and $l_2 = 2$, therefore

$$L = (2 + 2), \ (2 + 2 - 1) \ \text{.......} \ (2 - 2)$$

$$L = 4, 3, 2, 1, 0$$

$$\text{States} = G, F, D, P, S$$

Although the above-mentioned procedure provides the resultant orbital angular momentum quantum number (L) quite easily, the exact concept of orbital-orbital coupling can be understood only after knowing the concepts of space quantization. One thing that is totally clear is that these symbols are nothing but the mathematical shorthand of the electronic arrangements around the nucleus. The quantization of individual orbital angular momentums can be used to calculate the resultant value as follows:

i) For p^1p^1-configuration, $l_1 = 1$ and $l_2 = 1$, therefore orbital angular momentum for each of the electron is $\sqrt{2}$ and it is a well-known fact from the quantum mechanics that $\sqrt{2}$ angular momentum can be oriented in space with three different ways (+1, 0 and −1). The different combinations of orbital angular momentum can be calculated as

$l_1(z)$	=	+1	+1	+1	0	0	0	−1	−1	−1
$l_2(z)$	=	+1	0	−1	+1	0	−1	+1	0	−1
L_z	=	+2	+1	0	+1	0	−1	0	−1	−2

Hence, the orbital angular momentums of two p-electrons can interact in nine ways, creating nine combinations; out of which, three quantum-mechanically allowed series can be fashioned.

$$L_z = (+2, +1, 0, -1, -2), (+1, 0, -1), (0)$$

or

$$L = 2, 1, 0$$

Hence

$$\text{States} = D, P, S$$

Therefore, we can say that there are nine ways in which the orbital motion can interact.

Similarly,

ii) For d^1d^1-configuration, $l_1 = 2$ and $l_2 = 2$, therefore orbital angular momentum for each of the electron is $\sqrt{6}$ and it is a well-known fact from the quantum mechanics that $\sqrt{6}$ angular momentum can be oriented in space with five different ways (+2, +1, 0, −1 and −2). The different combinations of orbital angular momentum can be calculated as:

$l_1(z)$	=	+2	+2	+2	+2	+2	+1	+1	+1	+1	+1
$l_2(z)$	=	+2	+1	0	−1	−2	+2	+1	0	−1	−2
L_z	=	+4	+3	+2	+1	0	+3	+2	+1	0	−1

and

$l_1(z)$	=	0	0	0	0	0	−1	−1	−1	−1	−1
$l_2(z)$	=	+2	+1	0	+1	−2	+2	+1	0	−1	−2
L_z	=	+2	+1	0	−1	−2	+1	0	−1	−2	−3

and

$l_1(z)$	=	−2	−2	−2	−2	−2
$l_2(z)$	=	+2	+1	0	+1	−2
L_z	=	0	−1	−2	−3	−4

Hence, the orbital angular momentums of two d-electrons can interact in twenty-five ways, creating twenty-five combinations; out of which, five quantum-mechanically allowed series can be fashioned.

$$L_z = (+4, +3, +2, +1, 0, −1, −2, −3, −4), (+3, +2, +1, 0, −1, −2, −3), (+2, +1, 0, −1, −2), (+1, 0, −1), (0)$$

or

$$L = 4, 3, 2, 1, 0$$

Which means

$$\text{States} = G, F, D, P, S$$

2. Spin-spin coupling (s-s interaction): Consider a multielectron system, then the resultant spin angular momentum quantum number can be deduced as:

$$S = (s_1 + s_2), (s_1 + s_2 −1) \ldots\ldots |s_1 − s_2|$$

Where s_1 and s_2 are the individual spin angular momentum quantum numbers for electrons and modulus sign shows that the value of resultant spin angular momentum quantum number is always positive.

i) For p^1p^1 or d^1d^1-configuration, $s_1 = 1/2$ and $s_2 = 1/2$, therefore

$$S = (1/2 + 1/2), (1/2 - 1/2)$$

or

$$S = 1, 0$$

Which means

$$\text{Multiplicity} = (2S + 1) = 3 \text{ and } 1$$

   The aforementioned procedure offers the resultant spin angular momentum quantum number (S) quite easily but the exact concept of spin-spin interaction can be understood only after knowing the concepts of space quantization. The quantization of individual spin angular momentums can be used to calculate the resultant value as follows:

i) For p^1p^1 or d^1d^1-configuration, $s_1 = 1/2$ and $s_2 = 1/2$, therefore spin angular momentum for each of the electrons is $\sqrt{0.75}$ and it is a well-known fact from the quantum mechanics that $\sqrt{0.75}$ angular momentum can be oriented in space with two different ways ($+1/2$ and $-1/2$). The different combinations of spin angular momentum can be calculated as:

$s_1(z)$	=	+1/2	+1/2	−1/2	−1/2
$s_2(z)$	=	+1/2	−1/2	+1/2	−1/2
S_z	=	+1	0	0	−1

Hence, the spin angular momentums of two p or d-electrons can interact in four ways, creating four combinations; out of which, two quantum-mechanically allowed series can be fashioned.

$$S_z = (+1, 0, -1), (0)$$

or

$$S = 1, 0$$

$$\text{Multiplicity} = (2S + 1) = 3 \text{ and } 1$$

The multiplicity actually represents the number of orientations possible for the total spin relative to the total orbital angular momentum L, and thus to the number of near-degenerate levels that differ only in their spin-orbit coupling energy. For example, the ground state of the carbon atom is a ^3P state. The superscript of three specifies that the multiplicity $2S+1 = 3$ i.e. triplet, so that the total spin $S = 1$. This spin is due to two unpaired electrons, as a result of Hund's rule which favors the single filling of degenerate orbitals. The spin multiplicity is a primary factor in governing the overall energy of an electronic state and maybe summarised for different electron combination.

Table 3. Spin multiplicities for the different number of unpaired electron in an electronic configuration.

Unpaired Electrons	S	2S+1	State
0	0	1	Singlet
1	1/2	2	Doublet
2	1	3	Triplet
3	3/2	4	Quartet
4	2	5	Quintet

3. Spin-orbital coupling (L-S interaction): In a multi-electron system, the resultant orbital angular momentum (L) and resultant spin angular momentum (S) interact with each other to give total angular momentum which is defined by the quantum number J.

$$J = (L + S), (L + S - 1) \ldots\ldots |L - S|$$

Where L and S are the quantum numbers for resultant orbital angular momentum and resultant spin angular momentum, respectively. The modulus sign shows that the value of the resultant total angular momentum quantum number is always positive. The value of J is assigned as the subscripts of the overall term symbol.

i) For p^1p^1-configuration, 9 combinations given by orbital-orbital coupling (L = 2, 1, 0) and 4 combinations given by spin-spin coupling (S = 1, 0) combine to create a total of 36 microstates. therefore

$$L = 0, 1, 2 \text{ and } S = 1, 0$$

$$\text{States} = {}^3S, {}^3P, {}^3D, {}^1S, {}^1P, {}^1D$$

The summarization of spin-orbital coupling for p^1p^1-configurations is given below.

Table 4. Splitting of the term symbols for p^1p^1-configuration due to L-S coupling.

State	Value L and S	Value of J	States after L-S coupling
${}^3S$	L = 0 and S =1	J = (0 + 1) = 1	${}^3S_1$
${}^3P$	L = 1 and S = 1	J = (1 + 1) ….(1 − 1) = 2, 1, 0	${}^3P_2, {}^3P_1, {}^3P_0$
${}^3D$	L = 2 and S = 1	J = (2 + 1) ….(2 − 1) = 3, 2, 1	${}^3D_3, {}^3D_2, {}^3D_1$

Table 4. Continued on the next page…

^1S	$L = 0$ and $S = 0$	$J = (0 + 0) = 0$	$^1S_0$
^1P state:	$L = 1$ and $S = 0$	$J = (1 + 0) = 1$	$^1P_1$
^1D state:	$L = 2$ and $S = 0$	$J = (2 + 0) = 2$	$^1D_2$

ii) For d^1d^1-configuration, 25 combinations given by orbital-orbital coupling ($L = 4, 3, 2, 1, 0$) and 4 combinations given by spin-spin coupling ($S = 1, 0$) couple to create a total of 100 microstates. therefore

$$L = 4, 3, 2, 1, 0$$

$$S = 1, 0$$

$$\text{States} = {}^3S, {}^3P, {}^3D, {}^3F, {}^3G, {}^1S, {}^1P, {}^1D, {}^1F, {}^1G$$

The summarization of spin-orbital coupling for d^1d^1-configurations is given below.

Table 5. Splitting of the term symbols for d^1d^1-configuration due to L-S coupling.

State	Value L and S	Value of J	States after L-S coupling
^3S	$L = 0$ and $S = 1$	$J = (0 + 1) = 1$	$^3S_1$
^3P	$L = 1$ and $S = 1$	$J = (1 + 1) ... (1 - 1) = $ 2, 1, 0	$^3P_2, {}^3P_1, {}^3P_0$
^3D	$L = 2$ and $S = 1$	$J = (2 + 1) ... (2 - 1) = $ 3, 2, 1	$^3D_3, {}^3D_2, {}^3D_1$
^3F	$L = 3$ and $S = 1$	$J = (3 + 1) ... (3 - 1) = $ 4, 3, 2	$^3F_4, {}^3F_3, {}^3F_2$
^3G	$L = 4$ and $S = 1$	$J = (4 + 1) ... (4 - 1) = $ 5, 4, 3	$^3G_5, {}^3G_4, {}^3G_3$
^1S	$L = 0$ and $S = 0$	$J = (0 + 0) = 0$	$^1S_0$
^1P	$L = 1$ and $S = 0$	$J = (1 + 0) = 1$	$^1P_1$
^1D	$L = 2$ and $S = 0$	$J = (2 + 0) = 2$	$^1D_2$
^1F	$L = 3$ and $S = 0$	$J = (3 + 0) = 3$	$^1F_3$
^1G	$L = 4$ and $S = 0$	$J = (4 + 0) = 4$	$^1G_4$

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The quantization of individual orbital angular momentums can be used to calculate the resultant value as follows: For ^3P state of p^1p^1-configuration, L = 1 and S = 1. Therefore, the different combinations of resultant orbital angular momentum and resultant spin angular momentum can be calculated:

L_z	=	+1	+1	+1	0	0	0	−1	−1	−1
S_z	=	+1	0	−1	+1	0	−1	+1	0	−1
J_z	=	+2	+1	0	+1	0	−1	0	−1	−2

Hence, the resultant orbital angular momentums and resultant spin angular momentums of ^3P can interact in nine ways, creating nine microstates; out of which, three quantum-mechanically allowed series can be fashioned.

$$J_z = (+2, +1, 0, -1, -2), (+1, 0, -1), (0)$$

or

$$J = 2, 1, 0$$

Which means

$$\text{States} = {}^3P_2, {}^3P_1 \text{ and } {}^3P_0$$

> ➢ **Derivation of the Term Symbols for Unpaired Electrons in the Same Subshell**

In the previous section, we have distributed all the 36 microstates for p^1p^1-configuration in six electronic states labeled by $^3S, {}^3P, {}^3D, {}^1S, {}^1P$ and ^1D term symbols. However, for p^2-configuration (both of the unpaired electrons in same subshell), many microstates that were possible in p^1p^1-configuration cannot exist if they violate the Pauli exclusion principle. Therefore, there are only 15 microstates (complying with Pauli principle) for p^2-configuration which can be distributed in three electronic states labeled by $^1S, {}^3P$ and ^1D term symbols.

Similarly, all the 100 microstates for d^1d^1-configuration ($^3S, {}^3P, {}^3D, {}^3F, {}^3G, {}^1S, {}^1P, {}^1D, {}^1F$ and ^1G) cannot exist if they both the electrons are present in the same d-subshell. Therefore, there are only 45 microstates (complying with Pauli principle) for d^2-configuration which can be distributed in five electronic states labeled by $^1S, {}^3P, {}^1D, {}^3F$ and ^1G term symbols.

Term symbols for electronic configurations with unpaired electrons in the same subshell can be derived using "pigeon hole" diagrams. The principal steps for such operations are:

1. Create vertical columns for all allowed orientation or effect of individual orbital angular momentum in the reference direction. For example, +1, 0 and −1 are the allowed orientations of the orbital angular momentum corresponding to $l = 1$ value.

2. Fill up the electrons in these columns by exhausting all the possibilities of parallel, paired and opposite orientations.

3. Sum-up all the l_z values of every column to find out the resultant L_z values.

4. Quantum mechanically allowed series set-up should be carried out for different parallel, paired and opposite orientation, which in turn can be used to provide the resultant orbital angular momentum quantum number L for particular resultant spin quantum number S.

5. Combine the values of L and S to find out the term symbols for allowed electronic states.

1. s^1-configuration:

l_z

0 | ↑ |

L_z 0

As $L_z = 0$, the value of resultant orbital angular momentum quantum number L = 0. There is only one unpaired electron, therefore S = 1/2.

From L = 0, the state is S; and from S = 1/2, the multiplicity is 2. Thus, the overall term symbol is ^{2}S.

2. s^2-configuration:

l_z

0 | ↑↓ |

L_z 0

As $L_z = 0$, the value of resultant orbital angular momentum quantum number L = 0. There are no unpaired electrons, therefore S = 0.

From L = 0, the state is S; and from S = 0, the multiplicity is 1. Thus, the overall term symbol is ^{1}S.

3. p^1 and p^5-configuration:

l_z

−1 | | | ↑ |

0 | | ↑ | |

+1 | ↑ | | |

L_z +1   0   −1

As $L_z = +1, 0, −1$; the value of resultant orbital angular momentum quantum number L = 1. There is one unpaired electron, therefore S = 1/2.

From L = 1, the state is P; and from S = 1/2, the multiplicity is 2. Thus, the overall term symbol is ^{2}P. Hence, all the 6 microstates for p^1 and p^5-configurations are distributed in ^{2}P term symbol.

4. p^2 and p^4-configuration:

For parallel arrangements,

l_z

	L_z		
−1		↑	↑
0	↑		↑
+1	↑	↑	
L_z	+1	0	−1

As $L_z = +1, 0, -1$; the value of resultant orbital angular momentum quantum number $L = 1$.

There are two unpaired electrons, therefore $S = 1$.

From $L = 1$, the state is P.

From $S = 1$, the multiplicity is 3.

Thus, the overall term symbol is ^3P.

Similarly,

For paired and opposite arrangements,

l_z

−1		↑↓		↓		↓
0		↑↓		↓		↑
+1	↑↓			↑		↑
L_z	+2	0	−2	+1	0	−1

Out of six values of L_z (resultant orbital angular momentum in reference direction), two quantum-mechanically allowed series can be setup. One with $L_z = +2, +1, 0, -1, -2$; giving resultant orbital angular momentum quantum number $L = 2$. The second series with $L_z = 0$; giving resultant orbital angular momentum quantum number $L = 0$.

There are zero unpaired electrons, therefore $S = 0$.

From $L = 2$ and 0; the states are D and S, respectively.

From $S = 0$, the multiplicity is 1.

Thus, the overall term symbols are ^1D and ^1S.

Hence, all the 15 microstates for p^2 and p^4 electronic configurations which can be distributed in ^1S, ^3P and ^1D term symbols.

5. p^3-configuration:

l_z

−1	↑		↑	↑		↑↓	↑↓	↓	↓
0	↑	↑		↑↓	↑↓		↑	↑	↓
+1	↑	↑↓	↑↓		↑	↑		↑	↑

L_z 0   +2   +1   −1   +1   −1   −2   0   0

Parallel   Paired and opposite

For parallel arrangements,

As $L_z = 0$; the value of resultant orbital angular momentum quantum number $L = 0$. There are three unpaired electrons, therefore $S = 3/2$.

From $L = 0$, the state is S; and from $S = 3/2$, the multiplicity is 4. Thus, the overall term symbol is ^{4}S.

For paired and opposite arrangements,

Out of eight values of L_z, two quantum-mechanically allowed series can be setup. One with $L_z = +2, +1, 0, −1, −2$; giving resultant orbital angular momentum quantum number $L = 2$. The second series with $L_z = +1, 0, −1$; giving resultant orbital angular momentum quantum number $L = 1$. There is one unpaired electron, therefore $S = 1/2$.

From $L = 2$ and 1 the states are D and P, respectively.

From $S = 1/2$, the multiplicity is 2.

Thus, the overall term symbols are ^{2}D and ^{2}P.

Hence, all the 20 microstates for p^3-configurations are distributed in ^{4}S, ^{2}P and ^{2}D term symbols.

6. p^6-configuration:

l_z

−1	↑↓
0	↑↓
+1	↑↓

L_z 0

As $L_z = 0$, the value of resultant orbital angular momentum quantum number $L = 0$; and zero unpaired electrons, therefore $S = 0$. Thus, the overall term symbol is ^{1}S which contains the one and only microstate of p^6-electronic configuration.

---

7. d^1 and d^9-configuration:

l_z

	L_z +2	+1	0	−1	−2
−2					↑
−1				↑	
0			↑		
+1		↑			
+2	↑				

As L_z = +2, +1, 0, −1, −2; the value of resultant orbital angular momentum quantum number L = 2.

There is only one unpaired electron, therefore S = 1/2.

From L = 2, the state is D; and from S = 1/2, the multiplicity is also 2.

Thus, the overall term symbol is ^2D.

Hence, all the 10 microstates for d^1 and d^9-configurations are distributed in ^2D term symbols.

8. d^2 and d^8-configuration:

For parallel arrangements,

l_z

	L_z +3	+2	+1	0	+1	0	−1	−1	−2	−3
−2				↑			↑		↑	↑
−1			↑			↑		↑		↑
0		↑			↑			↑	↑	
+1	↑				↑	↑	↑			
+2	↑	↑	↑	↑						

Out of ten values of L_z, two quantum-mechanically allowed series can be setup. One with L_z = +3, +2, +1, 0, −1, −2, −3; giving resultant orbital angular momentum quantum number L = 3. The second series with L_z = +1, 0, −1; giving resultant orbital angular momentum quantum number L = 1. There are two unpaired electrons, therefore S = 1.

From L = 3 and 1, the states are F and P, respectively. From S = 1, the multiplicity is 3. Thus, the overall term symbols are ^3F and ^3P.

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For paired and opposite arrangements,

l_z

	+4	+2	0	−2	−4	+3	+2	+1	0	+1	0	−1	−1	−2	−3
−2					↑↓				↓			↓		↓	↓
−1				↑↓				↓			↓		↓		↑
0			↑↓				↓			↓			↑	↑	
+1		↑↓				↓				↑	↑	↑			
+2	↑↓					↑	↑	↑	↑						
L_z	+4	+2	0	−2	−4	+3	+2	+1	0	+1	0	−1	−1	−2	−3

Out of fifteen values of L_z, three quantum-mechanically allowed series can be setup. First with L_z = +4, +3, +2, +1, 0, −1, −2, −3, −4; giving resultant orbital angular momentum quantum number L = 4. Second series with L_z = +2, +1, 0, −1, −2; giving resultant orbital angular momentum quantum number L = 2. The third series with L_z = 0; giving resultant orbital angular momentum quantum number L = 0. There are zero unpaired electrons, therefore S = 0.

From L = 4, 2 and 0 the states are G, D and S, respectively. From S = 0, the multiplicity is 1. Thus, the overall term symbols are ^1G, ^1D and ^1S.

Hence, all the 45 microstates for d^2 and d^8-configurations are distributed in ^1S, ^3P, ^1D, ^3F and ^1G term symbols.

9. d^3 and d^7-configuration:

For parallel arrangements,

l_z

	+3	+2	+1	0	−1	−3	+1	−1	−2	0
−2			↑		↑	↑		↑	↑	↑
−1		↑		↑		↑	↑	↑	↑	
0	↑			↑	↑	↑	↑			↑
+1	↑	↑	↑	↑	↑				↑	
+2	↑	↑	↑				↑	↑		↑
L_z	+3	+2	+1	0	−1	−3	+1	−1	−2	0

Out of ten values of L_z, two quantum-mechanically allowed series can be setup.

One with L_z = +3, +2, +1, 0, −1, −2, −3; giving resultant orbital angular momentum quantum number L = 3.

The second series with L_z = +1, 0, −1; giving resultant orbital angular momentum quantum number L = 1. There are three unpaired electrons, therefore S = 3/2.

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From L = 3 and 1; the states are F and P, respectively. From S = 3/2, the multiplicity is 4. Thus, the overall term symbols are ^4F and ^4P.

For paired and opposite arrangements,

l_z															
−2				↑			↑			↑			↑		
−1			↑			↑			↑				↑↓	↑↓	↑↓
0		↑			↑				↑↓	↑↓	↑↓	↑↓		↑	
+1	↑				↑↓	↑↓	↑↓	↑↓			↑				↑
+2	↑↓	↑↓	↑↓	↑↓				↑				↑			
L_z	+5	+4	+3	+2	+2	+1	0	+4	−1	−2	+1	+2	−4	−2	−1

and

l_z															
−2		↑↓	↑↓	↑↓	↑↓		↓		↓		↑↓			↓	
−1	↑↓	↑				↓		↓		↓			↑↓		↑↓
0			↑							↑↓		↑↓		↑↓	
+1				↑				↑↓	↑↓		↓	↓	↓		
+2	↑				↑	↑↓	↑↓								↓
L_z	0	−5	−4	−3	−2	+3	+2	+1	0	−1	−3	+1	−1	−2	0

Out of thirty values of L_z, six quantum-mechanically allowed series can be setup. First with L_z = +5, +4, +3, +2, +1, 0, −1, −2, −3, −4, −5; giving resultant orbital angular momentum quantum number L = 5. Second series with L_z = +4, +3, +2, +1, 0, −1, −2, −3, −4; giving resultant orbital angular momentum quantum number L = 4. The third series with L_z = +3, +2, +1, 0, −1, −2, −3; giving resultant orbital angular momentum quantum number L = 3. Fourth and fifth series with L_z = +2, +1, 0, −1, −2; giving resultant orbital angular momentum quantum number L = 2 and 2, respectively. The sixth series is consisted of L_z = +1, 0, −1; giving resultant orbital angular momentum quantum number L = 1.

There is one unpaired electron, therefore S = 1/2.

From L = 5, 4, 3, 2, 2 and 1; the states are H, G, F, D, D and P, respectively.

From S = 1/2, the multiplicity is 2.

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Thus, the overall term symbols are ^2H, ^2G, ^2F, ^2D, ^2D and ^2P.

Hence, all the 120 microstates for d^3 and d^7-configurations are distributed in ^4F, ^4P, ^2H, ^2G, ^2F, ^2D, ^2D and ^2P term symbols.

10. d^4 and d^6-configuration:

For parallel arrangements,

l_z					
−2		↑	↑	↑	↑
−1	↑		↑	↑	↑
0	↑	↑		↑	↑
+1	↑	↑	↑		↑
+2	↑	↑	↑	↑	
L_z	+2	+1	0	−1	−2

Out of five values of L_z, only one quantum-mechanically allowed series can be set up with $L_z = +2, +1, 0, −1, −2$; giving resultant orbital angular momentum quantum number $L = 2$.

There are four unpaired electrons, therefore $S = 2$.

From $L = 2$, the state is D.

From $S = 2$, the multiplicity is 5.

Thus, the overall term symbol is ^5D.

For two electrons paired or opposite arrangement,

l_z															
−2			↑		↑	↑		↑	↑			↑	↑		
−1		↑	↑	↑		↑	↑		↑		↑		↑		↑
0	↑			↑	↑		↑	↑		↑			↑↓	↑↓	↑↓
+1	↑	↑	↑				↑↓	↑↓	↑↓	↑↓	↑↓	↑↓		↑	
+2	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓				↑	↑	↑		↑	↑
L_z	+5	+4	+2	+3	+2	+1	+1	0	−1	+4	+3	+2	−3	+3	+1

and

l_z

−2	↑		↑			↑		↑	↑	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
−1		↑		↑↓	↑↓	↑↓	↑↓	↑↓	↑↓			↑		↑	↑
0	↑↓	↑↓	↑↓		↑		↑		↑		↑		↑		↑
+1		↑	↑	↑			↑	↑		↑			↑	↑	
+2	↑			↑	↑	↑			↑	↑	↑				
L_z	0	0	−1	+1	0	−2	−1	−3	−4	−1	−2	−3	−3	−4	−5

and

l_z

−2		↓	↓	↓	↓		↑	↑	↑		↑	↑	↑	↑
−1	↓		↑	↑	↑	↑	↓	↓	↑		↑	↑	↑	
0	↑	↑	↑	↑	↓	↑	↑	↑	↑	↑		↓	↓	
+1	↑	↑	↑	↑	↑	↑	↓	↑	↓	↓	↓		↑	
+2	↑	↑	↑	↑	↑	↑	↑		↑	↑	↑	↑		
L_z	+2	+1	0	−1	−2	+2	+1	0	−1	−2	+2	+1	0	−1	−2

Out of forty-five values of L_z, seven quantum-mechanically allowed series can be setup as. First with $L_z = +5$, +4, +3, +2, +1, 0, −1, −2, −3, −4, −5; giving resultant orbital angular momentum quantum number $L = 5$. Second series with $L_z = +4, +3, +2, +1, 0, −1, −2, −3, −4$; giving resultant orbital angular momentum quantum number $L = 4$. The third and fourth series with $L_z = +3, +2, +1, 0, −1, −2, −3$; giving resultant orbital angular momentum quantum number $L = 3$ and 3. fifth series with $L_z = +2, +1, 0, −1, −2$; giving resultant orbital angular momentum quantum number $L = 2$. The sixth and seventh series is consisted of $L_z = +1, 0, −1$; giving resultant orbital angular momentum quantum number $L = 1$ and 1, respectively.

There are two unpaired electrons, therefore $S = 1$.

From $L = 5, 4, 3, 3, 2, 1$ and 1; the states are H, G, F, F, D, P and P, respectively.

From $S = 1$, the multiplicity is 3.

Thus, the overall term symbols are ^3H, ^3G, ^3F, ^3F, ^3D, ^3P and ^3P.

Similarly,

For all electrons paired or opposite arrangement,

l_z

−2				↑↓			↑↓		↑↓	↑↓			↓		↓
−1			↑↓		↑↓		↑↓		↑↓			↓		↓	
0		↑↓			↑↓			↑↓	↑↓		↓			↑	↑
+1	↑↓				↑↓	↑↓	↑↓				↑	↑	↑		
+2	↑↓	↑↓	↑↓	↑↓							↑↓	↑↓	↑↓	↑↓	↑↓
L_z	+6	+4	+2	0	+1	0	−2	−2	−4	−6	+5	+4	+2	+3	+2

and

l_z

−2	↓		↓	↓			↓		↓			↓		↓	
−1	↑	↓		↑		↓		↑		↓			↓	↑↓	↑↓
0		↑	↑		↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓		↓
+1		↑↓	↑↓	↑↓	↑↓	↑↓	↑↓		↓			↑	↑	↓	
+2	↑↓				↑	↑	↑			↑	↑	↑		↑	↑
L_z	+1	+1	0	−1	+4	+3	+2	−3	+3	+1	0	0	−1	+1	0

and

l_z

−2	↓		↓	↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓		↓	↓	↓	↓
−1	↑↓	↑↓	↑↓	↑↓			↓		↓	↓	↓		↓	↓	↓
0		↓		↑		↓		↓		↑	↓	↓		↑	↑
+1		↑	↑		↓			↑	↑		↑	↑	↑		↑
+2	↑				↑	↑	↑				↑	↑	↑	↑	↑
L_z	−2	−1	−3	−4	−1	−2	−3	−3	−4	−5	+2	+1	0	−1	−2

and

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l_z

	+2	+1	0	−1	−2
−2		↓	↓	↓	↓
−1	↓		↑	↑	↑
0	↑	↑		↓	↓
+1	↓	↓	↓		↑
+2	↑	↑	↑	↑	

L_z +2   +1   0   −1   −2

Out of fifty values of L_z, eight quantum-mechanically allowed series can be setup as. First with L_z = +6, +5, +4, +3, +2, +1, 0, −1, −2, −3, −4, −5, −6; giving resultant orbital angular momentum quantum number L = 6. Second and third series with L_z = +4, +3, +2, +1, 0, −1, −2, −3, −4; giving resultant orbital angular momentum quantum number L = 4 and 4, respectively. The fourth series with L_z = +3, +2, +1, 0, −1, −2, −3; giving resultant orbital angular momentum quantum number L = 3. Fifth and sixth series with L_z = +2, +1, 0, −1, −2; giving resultant orbital angular momentum quantum number L = 2 and 2, respectively. The seventh and eighth series is consisted of L_z = 0; giving resultant orbital angular momentum quantum number L = 0 and 0, respectively. There are zero unpaired electrons, therefore S = 0.

From L = 6, 4, 4, 3, 2, 2, 0 and 0; the states are I, G, G, F, D, D, S and S, respectively. From S = 0, the multiplicity is 1. Thus, the overall term symbols are ^1I, ^1G, ^1G, ^1F, ^1D, ^1D, ^1S and ^1S.

Hence, all the 210 microstates for d^4 and d^6-configurations are distributed in ^5D, ^3H, ^3G, ^3F, ^3F, ^3D, ^3P, ^3P, ^1I, ^1G, ^1G, ^1F, ^1D, ^1D, ^1S and ^1S term symbols.

11. d^5-configuration:

For parallel arrangements,

l_z

−2	↑
−1	↑
0	↑
+1	↑
+2	↑

L_z 0

As $L_z = 0$; the value of resultant orbital angular momentum quantum number $L = 0$. There are five unpaired electrons, therefore $S = 5/2$.

From $L = 0$, the state is S. From $S = 5/2$, the multiplicity is 6. Thus, the overall term symbol is ^{6}S.

For two electrons paired or opposite arrangement,

l_z

−2		↑	↑	↑		↑	↑	↑		↑	↑	↑		↑	↑
−1	↑		↑	↑	↑		↑	↑	↑		↑	↑	↑↓	↑↓	↑↓
0	↑	↑		↑	↑	↑		↑	↑↓	↑↓	↑↓	↑↓	↑		↑
+1	↑	↑	↑		↑↓	↑↓	↑↓	↑↓	↑	↑		↑	↑	↑	
+2	↑↓	↑↓	↑↓	↑↓	↑	↑	↑		↑	↑	↑		↑	↑	↑
L_z	+4	+3	+2	+1	+3	+2	+1	−1	+2	+1	−1	−2	+1	−1	−2

and

l_z

−2	↑	↑↓	↑↓	↑↓	↑↓	↓	↑	↑	↑
−1	↑↓		↑	↑	↑	↑	↓	↑	↑
0	↑	↑		↑	↑	↑	↑	↓	↑
+1	↑	↑	↑		↑	↑	↑	↑	↓
+2		↑	↑	↑	↑	↑	↑	↑	↑
L_z	−3	−1	−2	−3	−4	0	0	0	0

Out of twenty-four values of L_z, four quantum-mechanically allowed series can be setup as. First with $L_z = +4$, +3, +2, +1, 0, −1, −2, −3, −4; giving resultant orbital angular momentum quantum number $L = 4$. Second series with $L_z = +3$, +2, +1, 0, −1, −2, −3; giving resultant orbital angular momentum quantum number $L = 3$. The third series with $L_z = +2$, +1, 0, −1, −2; giving resultant orbital angular momentum quantum number $L = 3$. The fourth series is consisted of $L_z = +1$, 0, −1; giving resultant orbital angular momentum quantum number $L = 1$.

There are three unpaired electrons, therefore $S = 3/2$.

From $L = 4, 3, 2$ and 1; the states are G, F, D and P, respectively.

From $S = 3/2$, the multiplicity is 4.

Thus, the overall term symbols are ^{4}G, ^{4}F, ^{4}D and ^{4}P.

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For four electrons paired or opposite arrangement,

l_z															
−2			↑			↑			↑	↑↓	↑↓	↑↓			↑
−1		↑			↑		↑↓	↑↓	↑↓			↑		↑	
0	↑			↑↓	↑↓	↑↓		↑			↑		↑↓	↑↓	↑↓
+1	↑↓	↑↓	↑↓	↑			↑			↑			↑↓	↑↓	↑↓
+2	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑		
L_z	+6	+5	+4	+5	+3	+2	+3	+2	0	+1	0	−1	+4	+1	0

and

l_z															
−2			↑	↑↓	↑↓	↑↓		↑	↑↓	↑↓	↑↓		↑↓	↑↓	↑↓
−1	↑↓	↑↓	↑↓		↑	↑↓	↑↓	↑↓			↑		↑↓	↑↓	↑↓
0		↑			↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓				↑
+1	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓				↑			↑	
+2	↑		↑			↑		↑		↑			↑		
L_z	+2	0	−2	0	−2	−3	0	−1	−4	−2	−3	−5	−4	−5	−6

and

l_z															
−2		↓	↓	↓		↓	↓	↓		↓	↓	↓		↓	↓
−1	↓		↑	↑	↓		↑	↑	↓		↑	↑	↑↓	↑↓	↑↓
0	↑	↑		↑	↑	↑		↑	↑↓	↑↓	↑↓	↑↓	↓		↑
+1	↑	↑	↑		↑↓	↑↓	↑↓	↑↓	↑	↑		↑	↑	↑	
+2	↑↓	↑↓	↑↓	↑↓	↑	↑	↑		↑	↑	↑		↑	↑	↑
L_z	+4	+3	+2	+1	+3	+2	+1	−1	+2	+1	−1	−2	+1	−1	−2

and

l_z

l_z															
−2	↓	↑↓	↑↓	↑↓	↑↓		↑	↑	↑		↑	↑	↑		↑
−1	↑↓		↓	↓	↓	↑		↓	↓	↑		↓	↓	↑	
0	↑	↓		↑	↑	↓	↓		↑	↓	↓		↑	↑↓	↑↓
+1	↑	↑	↑		↑	↑	↑	↑		↑↓	↑↓	↑↓	↑↓	↓	↓
+2		↑	↑	↑		↑↓	↑↓	↑↓	↑↓	↑	↑	↑		↑	↑
L_z	−3	−1	−2	−3	−4	+4	+3	+2	+1	+3	+2	+1	−1	+2	+1

and

l_z

l_z															
−2	↑	↑		↑	↑	↑↓	↑↓	↑↓	↑↓	↓	↑	↑	↑	↑	
−1	↓	↓	↑↓	↑↓	↑↓	↑↓		↑	↑	↓	↓	↑	↑	↓	
0	↑↓	↑↓	↑	↓	↑	↓	↓	↓	↑	↓	↑	↑		
+1		↑	↓	↓	↓	↑	↑	↓	↓	↓				
+2	↑		↑	↑	↑	↑	↑	↑	↓	↑	↑	↓	↑	
L_z	−1	−2	+1	−1	−2	−3	−1	−2	−3	−4	0	0	0	0	0

Out of seventy-five values of L_z, eleven quantum-mechanically allowed series can be setup. First with $L_z = +6$, +5, +4, +3, +2, +1, 0, −1, −2, −3, −4, −5, −6; giving resultant orbital angular momentum quantum number $L = 6$. Second series with $L_z = +5$, +4, +3, +2, +1, 0, −1, −2, −3, −4 −5; giving resultant orbital angular momentum quantum number $L = 5$. The third and fourth series with $L_z = +4$, +3, +2, +1, 0, −1, −2, −3, −4; giving resultant orbital angular momentum quantum number $L = 4$. Fifth and sixth series with $L_z = +3$, +2, +1, 0, −1, −2, −3; giving resultant orbital angular momentum quantum number $L = 3$ and 3, respectively. The seventh, eighth and ninth series are consisted of $L_z = +2$, +1, 0, −1, −2; giving resultant orbital angular momentum quantum number $L = 2$, 2 and 2, respectively. The tenth and eleventh series are consisted of $L_z = +1$, 0, −1 and $L_z = 0$; giving resultant orbital angular momentum quantum number $L = 1$ and 0, respectively.

There is one unpaired electron which $S = 1/2$.

From $L = 6, 5, 4, 4, 3, 3, 2, 2, 2, 1$ and 0; the states are I, H, G, G, F, F, D, D, D, P and S, respectively. From $S = 1/2$, the multiplicity is 2. Thus, the overall term symbols are ^2I, ^2H, ^2G, ^2G, ^2F, ^2F, ^2D, ^2D, ^2D, ^2P and ^2S.

Hence, all the 252 microstates for d^5-configurations are distributed in ^2I, ^2H, ^2G, ^2G, ^2F, ^2F, ^2D, ^2D, ^2D, ^2P, ^2S, ^4G, ^4F, ^4D, ^4P and ^6S term symbols.

12. d^{10}-configuration:

l_z

-2	↑↓
-1	↑↓
0	↑↓
$+1$	↑↓
$+2$	↑↓

L_z 0

As $L_z = 0$; the value of resultant orbital angular momentum quantum number $L = 0$. There are no unpaired electrons, therefore $S = 0$.

From $L = 0$, the state is S. From $S = 0$, the multiplicity is 1. Thus, the overall term symbol is ^1S which contains the only microstate of d^{10}-configuration.

      It can clearly be seen that the number of microstates, as well as the term symbols for dn and d10−n configurations, are the same. This is due to the fact that the number of unpaired electrons is the same for both of the configurations. In other words, the possible arrangements for unpaired electrons in less than half-filled or for holes in more than half-filled configurations are the same. The same analogy is true for s, p or f-subshell.

      Moreover, the number of microstates distributed in any term symbol can be calculated using the following relations:

1. Term symbols without J-value: $(2L+1) \times (2S+1)$

2. Term symbols without J-value: $(2J+1)$

Let us tally the number of microstates for p^2 electronic configuration with term symbols distribution.

		$(2L+1) \times (2S+1)$	$(2J+1)$
Distribution of 15 microstates of p^2-configuration in ^1S, ^3P, ^1D term symbols	$\rightarrow$	$^1S = (2 \times 0+1) \times (2 \times 0+1) = 1$ $^3P = (2 \times 1+1) \times (2 \times 1+1) = 9$ $^1D = (2 \times 2+1) \times (2 \times 0+1) = 5$	$^1S_0 = 2 \times 0 + 1 = 1$ $^3P_2 = 2 \times 2 + 1 = 5$ $^3P_1 = 2 \times 1 + 1 = 3$ $^3P_0 = 2 \times 0 + 1 = 1$ $^1D_2 = 2 \times 2 + 1 = 5$

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> ➤ *Determination of Spectroscopic Ground State Term*

In a particular configuration, the classification of various microstates in different term symbols also distinguishes them energetically. It can be explained in terms of the effect of spin-spin, orbital-orbital and spin-orbital coupling. There are two different approaches, both are based upon some conclusive results from quantum mechanics, to find out the term symbol for ground electronic state.

1. From correlation diagram: This approach is based on the correlation of all the free ion term of a particular atom or ion and then the ground state term is calculated with the help of certain rules.

i) The energy of different terms (electronic states) depends primarily on the Hund's rule, which states that the most stable state should have the highest multiplicity. Hence, triplet states are more stable than the singlet one. In other words, the higher the value of 2S+1, the greater will be the stability.

ii) If the value of spin multiplicities for two different states is the same, the value of resultant angular momentum will the deciding factor in the determination of the lower energy term. A higher value of L gives the lower energy state and the vice-versa is also true.

iii) The energy dependence of different terms upon total angular momentum is configuration-specific in nature. The perturbed Hamiltonian of spin-orbital interaction can have both types of effect, stabilization or destabilization, over the energy states and depends upon the magnitude of J-value. It has been proved that the interaction of spin-orbital motion destabilizes the less than half filed configuration and stabilizes the more than half-filled. Hence, a lower J-value for less than half-filled and a higher J-value of more than half will give the lower energy.

Let us apply this procedure to find out the ground state term symbol for p^2-configuration:
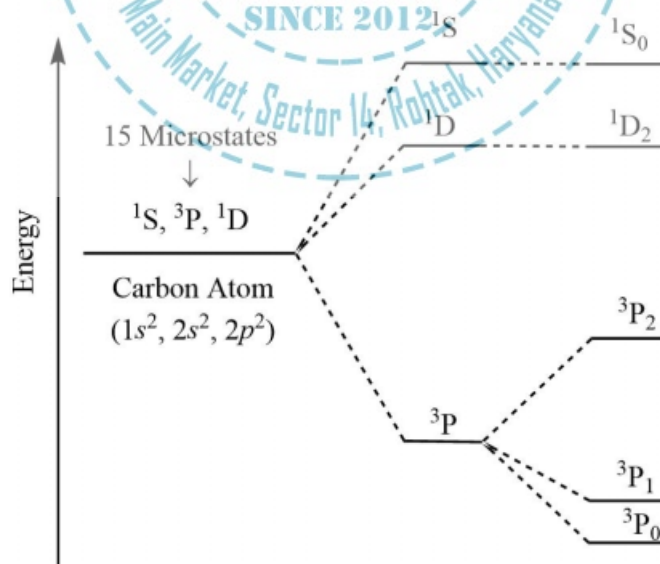
Figure 1. Splitting of free ion terms in the carbon atom.

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The effect of spin-spin interaction makes the triplet (^{3}P) state more stable in comparison to the singlet ^{1}D or ^{1}S. Furthermore, the stabilization of ^{1}D state after the consideration of orbital-orbital interaction can be attributed to the higher value of orbital angular momentum. Finally, as the p^2-configuration is less than half-filled; the splitting of ^{3}P state goes with ^{3}P$_0$ as the ground state term symbol.

2. Using L-S coupling scheme: This procedure is applicable only to find out the ground state term symbol. We do not need to calculate all the microstates but only present in the ground electronic state. Various steps involved in this procedure are:

1. The electron filling in the valence subshell should be carried out in such a way that a maximum spin multiplicity (2S+1) is produced.

2. Maximize the value of resultant orbital angular momentum component by filing electrons first in the orbitals with the positive component of individual orbital angular momentum.

3. Select maximum J-value for more than half-filled and minimum J-value for less than half-filled configuration.

Let us determine the ground state term symbol for carbon atom. The electronic configuration for carbon is $1s^2$, $2s^2$, $2p^2$.

$$l_z \quad\quad +1 \quad\quad 0 \quad\quad -1$$

$$2p \quad \boxed{\uparrow} \; \boxed{\uparrow} \; \boxed{}$$
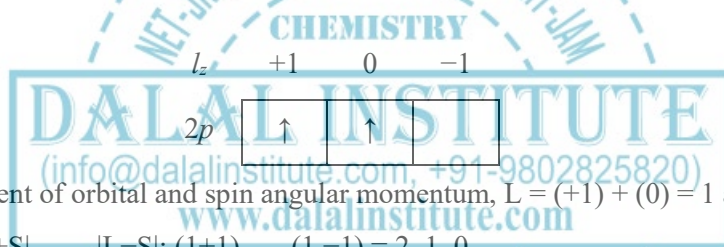
From the total component of orbital and spin angular momentum, L = (+1) + (0) = 1 and S = 1/2 + 1/2 = 1.

From L-S coupling, |L+S| ...... |L−S|; (1+1) …. (1 −1) = 2, 1, 0.

Now, as the configuration is less than half-filled, the lower J-value is selected for lower energy. Thus, this gives rise to a ^{3}P$_0$ state.

For nitrogen atom, the determination of the ground state term symbol can be calculated through the same route. The electronic configuration for nitrogen is $1s^2$, $2s^2$, $2p^3$.

$$l_z \quad\quad +1 \quad\quad 0 \quad\quad -1$$

$$2p \quad \boxed{\uparrow} \; \boxed{\uparrow} \; \boxed{\uparrow}$$
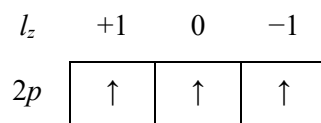
From the total component of orbital and spin angular momentum, L = (+1) + (0) + (−1) = 0 and S = 1/2 + 1/2 + 1/2 = 3/2.

From L-S coupling, |L+S| ..… |L−S|; (0 + 3/2) = 3/2.

Now, as the configuration is half-filled, the only J-value is bound to be selected for lower energy. Thus, this gives rise to a ^{4}S$_{3/2}$ state.

For trivalent vanadium ion (V^{3+}), the electronic configuration can be given as is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^0$, $3d^2$.

l_z	+2	+1	0	−1	−2
$3d$	↑	↑			

From the total component of orbital and spin angular momentum, L = (+2) + (+1) = 3 and S = 1/2 + 1/2 = 1.

From L-S coupling, |L+S| ...… |L−S|; (3 + 1) …. (3 − 1) = 4, 3, 2. Now, as the configuration is less than half-filled, the lower J-value is selected for lower energy. Thus, this gives rise to a $^3F_2$ state. However, the ground state term symbol for d^8-configuration will be $^3F_4$.

All the free ions terms (including ground states) for different electronic configurations are summarized in the following table. However, it must be kept in mind that the ground state term symbol after L-S coupling will be different for more than half-filled and less than half-filled counterparts.

Table 6. The free ion terms and the corresponding ground electronic states for different types of electronic configuration.

Electronic configuration	Free ion terms	Ground State
s^1	^2S	^2S
s^2	^1S	^1S
p^1, p^5	^2P	^2P
p^2, p^4	$^1S, ^3P, ^1D$	^3P
p^3	$^4S, ^2P, ^2D$	^4S
p^6	^1S	^1S
d^1, d^9	^2D	^2D
d^2, d^8	$^1S, ^3P, ^1D, ^3F, ^1G$	^3F
d^3, d^7	$^4F, ^4P, ^2H, ^2G, ^2F, ^2D, ^2D, ^2P$	^4F
d^4, d^6	$^5D, ^3H, ^3G, ^3F, ^3F, ^3D, ^3P, ^3P, ^1I, ^1G, ^1G, ^1F, ^1D, ^1D, ^1S, ^1S$	^5D
d^5	$^2I, ^2H, ^2G, ^2G, ^2F, ^2F, ^2D, ^2D, ^2D, ^2P, ^2S, ^4G, ^4F, ^4D, ^4P, ^6S$	^6S
d^{10}	^1S	^1S

It is also worthy to note that the ground state term symbol for all fully-filled subshells like s^2, p^6, or d^{10} is ^1S always which also includes the one and only microstate available.

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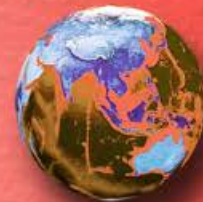
A TEXTBOOK OF INORGANIC CHEMISTRY

Volume I

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