



**Lt. Shree Cimanbhai Shukla**

**B. Sc. Chemistry Semester-5 – Chapter 1**  
**Multi electron system**

Shree H.N.Shukla College  
Campus, Street No. 2,  
Vaishali Nagar,  
Nr. Amrapali Railway  
Crossing, Raiya Road,  
Rajkot.  
Ph. (0281)2440478,  
2472590

Shree H.N.Shukla College  
Street No. 3, Vaishali  
Nagar, Nr. Amrapali  
Railway Crossing, Raiya  
Road, Rajkot.  
Ph. (0281)2440478,  
2472590

Shree H.N.Shukla College  
B/H Markeeting yard N/R  
Lalpari lake Bhichari Road  
Rajkot.  
Ph. (0281)2471645  
Mo, 9998381777,  
90990631550

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➤ **Quantum Numbers**

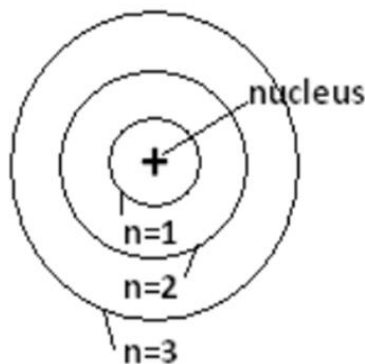
Quantum numbers is like Postal *addresses* for electrons in an atom. To post any letter or parcel, you would write the state → city → street → street number to tell the post office where to go. Quantum numbers also work with the same manner: energy level → type of orbital → orientation of orbital → orientation of electron.

**Each and every electron in the atom will have a unique set of quantum numbers in the form [n, l, ml, ms].**

➤ **Principal Quantum Number (n = 1, 2, 3, 4, ...∞)**

The principal quantum number, **n**, defines the energy level or shell of the electron. It is the first quantum number that must be determined, as it defines the available values for all other quantum numbers. Think of Bohr's model for the atom; **n** defines the circular orbit on which the electron resides.

The value of **n** gives information how many levels away from the nucleus the electron is. The valence shell of an atom is the **highest occupied shell** and is mathematically equivalent the period of the element (i.e., H is in period 1, so the valence shell for H is n = 1).



to

➤ **Azimuthal (Angular Momentum) Quantum Number (l = 0, 1, 2, ... (n-1) )**

The azimuthal, or angular momentum, quantum number, **l**, defines the *type* or *shape* of the orbital where the electron most probably resides. It is the second quantum number to be determined as its value relies only on **n** (i.e., if **n** = 2, then **l** = 0 or 1 since **n** - 1 = 1). Each type of orbital has a unique number of *nodes* (e.g., where the wave changes phases) which is mathematically equivalent to **l**.

If **l** = 0, the electron is in an **s-orbital** that has 0 nodes.

If **l** = 1, the electron is in a **p-orbital** that has 1 node.

If **l** = 2, the electron is in a **d-orbital** that has 2 nodes.

If **l** = 3, the electron is in an **f-orbital** that has 3 nodes.

➤ **Magnetic Quantum Number (ml = -l...0...+l)**

The magnetic quantum number, **ml**, defines the orientation of the orbital in which the electron inhabits. The number of **ml** values is called the degeneracy, or the number of orbitals in the atom that are at the same energy level. Note that to have the same energy, the orbitals must be on the same energy level as well as be the same type of orbital (**n** and **l** values are equal). A 2s orbital is not degenerate (e.g., the same energy) with a 2p or a 1s orbital.

The **ml** values are entirely dependent on the **l** values; each type of orbital has a set degeneracy.

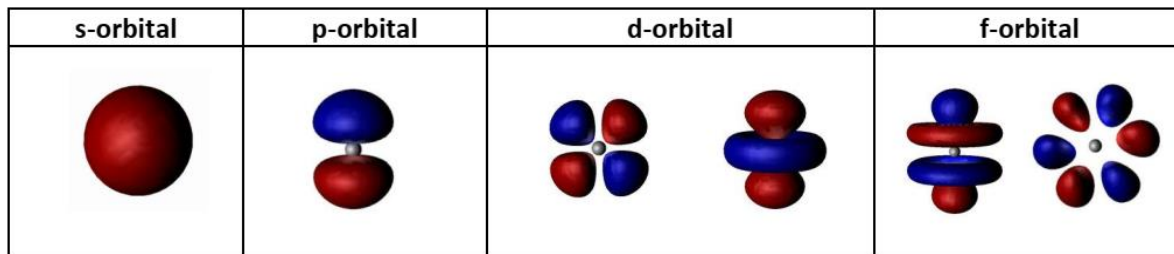
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For an s-orbital,  $m_l = 0$ , and degeneracy = 1.

For a p-orbital,  $m_l = -1, 0, +1$ , and degeneracy = 3.

For a d-orbital,  $m_l = -2, -1, 0, +1, +2$ , and degeneracy = 5.

For an f-orbital,  $m_l = -3, -2, -1, 0, +1, +2, +3$ , and degeneracy = 7.



**NOTE:** A set of 2p orbitals and 3p orbitals may have the same degeneracy value, but they are

**NOT** degenerate with each other. They both include three total orbitals, but they are not at the same energy: they have different  $n$  values.

➤ **Spin Quantum Number ( $m_s = -\frac{1}{2}, +\frac{1}{2}$ )**

The spin quantum number,  $m_s$ , is independent of the values of  $n$ ,  $l$ , and  $m_l$ . It is always  $+\frac{1}{2}$  for an electron who has its spin oriented *clockwise*, and  $-\frac{1}{2}$  for an electron who has its spin oriented *anticlockwise*. This state that there are **two electrons allowed per orbital, independent of energy level, shape, or orientation**. It is always denoted by  $m_s = \pm \frac{1}{2}$ .

➤ **TO SUMMARIZE:**

If $n$ is:	Then $l$ can be:	so $m_l$ is:	with a degeneracy of:	and $m_s$ as:
1	0	0	1	$-\frac{1}{2}, +\frac{1}{2}$
2	0 1	0 -1, 0, 1	1 3	$-\frac{1}{2}, +\frac{1}{2}$ $-\frac{1}{2}, +\frac{1}{2}$
3	0 1 2	0 -1, 0, 1 -2, -1, 0, 1, 2	1 3 5	$-\frac{1}{2}, +\frac{1}{2}$ $-\frac{1}{2}, +\frac{1}{2}$ $-\frac{1}{2}, +\frac{1}{2}$
4	0 1 2 3	0 -1, 0, 1 -2, -1, 0, 1, 2 -3, -2, -1, 0, 1, 2, 3	1 3 5 7	$-\frac{1}{2}, +\frac{1}{2}$ $-\frac{1}{2}, +\frac{1}{2}$ $-\frac{1}{2}, +\frac{1}{2}$ $-\frac{1}{2}, +\frac{1}{2}$

➤ **Review of Quantum Numbers**

Electrons in an atom reside in shells characterized by a particular value of  $n$ , the Principal Quantum Number. Within each shell an electron can occupy an orbital which is further characterized by an Orbital Quantum Number,  $l$ , where  $l$  can take all values in the range:

$l = 0, 1, 2, 3, \dots, (n-1)$ , traditionally termed s, p, d, f, etc. orbitals.

Each orbital has a characteristic shape reflecting the motion of the electron in that particular orbital, this motion being characterized by an angular momentum that reflects the angular velocity of the electron moving in its orbital. A quantum mechanics approach to determining the energy of electrons in an element or ion is based on the results obtained by solving the Schrödinger Wave Equation for the H-atom. The various solutions for the different energy states are characterized by the three quantum numbers,  $n$ ,  $l$  and  $m_l$ .

- $m_l$  is a subset of  $l$ , where the allowable values are:  $m_l = l, l-1, l-2, \dots, 1, 0, -1, \dots, -(l-2), -(l-1), -l$ .
- There are thus  $(2l + 1)$  values of  $m_l$  for each  $l$  value, i.e. one s orbital ( $l = 0$ ), three p orbitals ( $l = 1$ ), five d orbitals ( $l = 2$ ), etc.
- There is a fourth quantum number,  $m_s$ , that identifies the orientation of the spin of one electron relative to those of other electrons in the system. A single electron in free space has a fundamental property associated with it called spin, arising from the spinning of an asymmetrical charge distribution about its own axis. Like an electron moving in its orbital around a nucleus, the electron spinning about its axis has associated with its motion a well-defined angular momentum. The value of  $m_s$  is either  $+ \frac{1}{2}$  or  $- \frac{1}{2}$ .

In summary then, each electron in an orbital is characterized by four quantum numbers

<b>Table 1: Quantum Numbers</b>		
<b>symbol</b>	<b>description</b>	<b>range of values</b>
$n$	Principal Quantum Number - largely governs size of orbital and its energy	1,2,3 etc
$l$	Azimuthal/Orbital Quantum Number - largely determines shape of subshell 0 for s orbital, 1 for p orbital etc	$(0 \leq l \leq n-1)$ for $n = 3$ then $l = 0, 1, 2$ (s, p, d)
$m_l$	Magnetic Quantum Number - orientation of subshell's shape for example $p_x$ with $p_y$ and $p_z$	$l \geq m_l \geq -l$ for $l = 2$ , then $m_l = 2, 1, 0, -1, -2$
$m_s$	Spin Quantum Number	either $+ \frac{1}{2}$ or $- \frac{1}{2}$ for single electron

➤ **Russell Saunders coupling**

The ways in which the angular momenta associated with the orbital and spin motions in many-electron-atoms can be combined together are many and varied. In spite of this seeming complexity, the results are frequently readily determined for simple atom systems and are used to characterize the electronic states of atoms. The interactions that can occur are of three types.

- spin-spin coupling
- orbit-orbit coupling
- spin-orbit coupling

There are two principal coupling schemes used:

- Russell-Saunders (or L - S) coupling
- and jj coupling.

In the Russell Saunders scheme (named after Henry Norris Russell, 1877-1957 a Princeton Astronomer and Frederick Albert Saunders, 1875-1963 a Harvard Physicist and published in *Astrophysics Journal*, 61, 38, 1925).

It is assumed that:

spin-spin coupling > orbit-orbit coupling > spin-orbit coupling.

This is found to give a good approximation for first row transition series where spin-orbit (J) coupling can generally be ignored, however for elements with atomic number greater than thirty, spin-orbit coupling becomes more significant and the j-j coupling scheme is used.

➤ **Spin-Spin Coupling**

S - The resultant spin quantum number for a system of electrons. The overall spin S arises from adding the individual  $m_s$  together and is as a result of coupling of spin quantum numbers for the separate electrons.

➤ **Orbit-Orbit Coupling**

L - The total orbital angular momentum quantum number defines the energy state for a system of electrons. These states or term letters are represented as follows.

Total Orbital Momentum						
L	0	1	2	3	4	5
	S	P	D	F	G	H

➤ **Spin-Orbit Coupling**

Coupling occurs between the resultant spin and orbital momenta of an electron which gives rise to J the total angular momentum quantum number. Multiplicity occurs when several levels are close together and is given by the formula (2S+1). The Russell Saunders term symbol that results from these considerations is given by:

$$(2S+1)L(2)(2)(2S+1)L$$

Configuration

$$S = +\frac{1}{2}, \text{ hence } (2S+1) = 2$$

L=2 and the Ground Term is written as  ${}^2D$

The Russell Saunders term symbols for the other free ion configurations are given in the Table below.

<b>Terms for 3d<sup>n</sup> free ion configurations</b>				
<b>Configuration</b>	<b>No. of quantum states</b>	<b>No. of energy levels</b>	<b>No. Ground Term</b>	<b>No. Excited Terms</b>
d <sup>1</sup> , d <sup>9</sup>	10	1	<b><math>{}^2D</math></b>	-
d <sup>2</sup> , d <sup>8</sup>	45	5	<b><math>{}^3F</math></b>	<b><math>{}^3P, {}^1G, {}^1D, {}^1S</math></b>
d <sup>3</sup> , d <sup>7</sup>	120	8	<b><math>{}^4F</math></b>	<b><math>{}^4P, {}^2H, {}^2G, {}^2F, 2 \times {}^2D, {}^2P</math></b>
d <sup>4</sup> , d <sup>6</sup>	210	16	<b><math>{}^5D</math></b>	<b><math>{}^3H, {}^3G, 2 \times {}^3F, {}^3D, 2 \times {}^3P, {}^1I, 2 \times {}^1G, {}^1F, 2 \times {}^1D, 2 \times {}^1S</math></b>
d <sup>5</sup>	252	16	<b><math>{}^6S</math></b>	<b><math>{}^4G, {}^4F, {}^4D, {}^4P, {}^2I, {}^2H, 2 \times {}^2G, 2 \times {}^2F, 3 \times {}^2D, {}^2P, {}^2S</math></b>

Note that d<sup>n</sup> gives the same terms as d<sup>10-n</sup>

➤ **Hund's Rules**

The Ground Terms are deduced by using Hund's Rules. The two rules are:

1. The Ground Term will have the maximum multiplicity
2. If there is more than 1 Term with maximum multiplicity, then the Ground Term will have the largest value of L.

A simple graphical method for determining just the ground term alone for the free-ions uses a "fill in the boxes" arrangement.

$d^n$	2	1	0	-1	-2	L	S	Ground Term
$d^1$	↑					2	1/2	$^2D$
$d^2$	↑	↑				3	1	$^3F$
$d^3$	↑	↑	↑			3	3/2	$^4F$
$d^4$	↑	↑	↑	↑		2	2	$^5D$
$d^5$	↑	↑	↑	↑	↑	0	5/2	$^6S$
$d^6$	↑↓	↑	↑	↑	↑	2	2	$^5D$
$d^7$	↑↓	↑↓	↑	↑	↑	3	3/2	$^4F$
$d^8$	↑↓	↑↓	↑↓	↑	↑	3	1	$^3F$
$d^9$	↑↓	↑↓	↑↓	↑↓	↑	2	1/2	$^2D$

To calculate **S**, simply sum the **unpaired** electrons using a value of  $\frac{1}{2}$  for each. To calculate **L**, use the labels for each column to determine the value of **L** for that box, and then add all the individual box values together.

#### Configuration

For a  $d^7$  configuration, then:

- in the +2 box are 2 electrons, so **L** for that box is  $2*2=4$
- in the +1 box are 2 electrons, so **L** for that box is  $1*2=2$
- in the 0 box is 1 electron, **L** is 0
- in the -1 box is 1 electron, **L** is  $-1*1=-1$
- in the -2 box is 1 electron, **L** is  $-2*1=-2$

Total value of **L** is therefore  $+4 +2 +0 -1 -2$  or **L**=3. Note that for 5 electrons with 1 electron in each box then the total value of **L** is 0. This is why **L** for a  $d^1$  configuration is the same as for a  $d^6$ .

The other thing to note is the idea of the "hole" approach. A  $d^1$  configuration can be treated as similar to a  $d^9$  configuration. In the first case there is 1 electron and in the latter there is an absence of an electron i.e., a hole.

The overall result shown in the Table above is that:

- 4 configurations ( $d^1, d^4, d^6, d^9$ ) give rise to D ground terms,
- 4 configurations ( $d^2, d^3, d^7, d^8$ ) give rise to F ground terms
- and the  $d^5$  configuration gives an S ground term.



➤ **The Crystal Field Splitting of Russell-Saunders terms**

The effect of a crystal field on the different orbitals (s, p, d, etc.) will result in splitting into subsets of different energies, depending on whether they are in an octahedral or tetrahedral environment. The magnitude of the d orbital splitting is generally represented as a fraction of  $\Delta_{\text{oct}}$  or  $10Dq$ .

The ground term energies for free ions are also affected by the influence of a crystal field and an analogy is made between orbitals and ground terms that are related due to the angular parts of their electron distribution. The effect of a crystal field on different orbitals in an octahedral field environment will cause the d orbitals to split to give  $t_{2g}$  and  $e_g$  subsets and the D ground term states into  $T_{2g}$  and  $E_g$ , (where upper case is used to denote states and lower case orbitals). f orbitals are split to give subsets known as  $t_{1g}$ ,  $t_{2g}$  and  $a_{2g}$ . By analogy, the F ground term when split by a crystal field will give states known as  $T_{1g}$ ,  $T_{2g}$ , and  $A_{2g}$ .

Note that it is important to recognize that the F ground term here refers to states arising from d orbitals and not f orbitals and depending on whether it is in an octahedral or tetrahedral environment the lowest term can be either  $A_{2g}$  or  $T_{1g}$ .

<b>The Crystal Field Splitting of Russell-Saunders terms in high spin octahedral crystal fields.</b>	
<b>Russell-Saunders Terms</b>	<b>Crystal Field Components</b>
<b>S (1)</b>	$A_{1g}$
<b>P (3)</b>	$T_{1g}$
<b>D (5)</b>	$E_g, T_{2g}$
<b>F (7)</b>	$A_{2g}, T_{1g}, T_{2g}$
<b>G (9)</b>	$A_{1g}, E_g, T_{1g}, T_{2g}$
<b>H (11)</b>	$E_g, 2 \times T_{1g}, T_{2g}$
<b>I (13)</b>	$A_{1g}, A_{2g}, E_g, T_{1g}, 2 \times T_{2g}$

Note that, for simplicity, spin multiplicities are not included in the table since they remain the same for each term. The table above shows that the Mulliken symmetry labels, developed for atomic and molecular orbitals, have been applied to these states but for this purpose they are written in CAPITAL LETTERS.

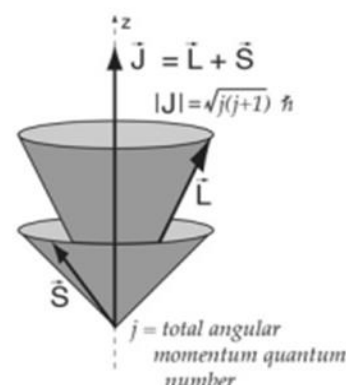
For splitting in a tetrahedral crystal field the components are similar, except that the symmetry label g (gerade) is absent. The ground term for first-row transition metal ions is either D, F or S which in high spin octahedral fields gives rise to A, E or T

states. This means that the states are either non-degenerate, doubly degenerate or triply degenerate.

Mulliken Symbols	
Mulliken Symbol for atomic and molecular orbitals	Explanation
<b>A</b>	Non-degenerate orbital; symmetric to principal $C_n$
<b>B</b>	Non-degenerate orbital; unsymmetric to principal $C_n$
<b>e</b>	Doubly degenerate orbital
<b>t</b>	Triply degenerate orbital
(subscript) <b>g</b>	Symmetric with respect to center of inversion
(subscript) <b>u</b>	Unsymmetric with respect to center of inversion
(subscript) <b>1</b>	Symmetric with respect to $C_2$ perp. to principal $C_n$
(subscript) <b>2</b>	Unsymmetric with respect to $C_2$ perp. to principal $C_n$
(superscript) <b>'</b>	Symmetric with respect to $s_h$
(superscript) <b>"</b>	Unsymmetric with respect to $s_h$

➤ **L-S coupling**

L-S coupling or Russell-Saunders coupling predicts results in good agreement with the observed spectral details for many light atoms. In such cases of multi-electron atoms the spin-orbit coupling is weak. In this coupling scheme it is presumed that the orbital angular momenta of the individual electrons add to form a resultant orbital angular momentum  $L$ . Similarly, the individual spin angular momenta should couple to produce a resultant spin angular momentum  $S$ . Then  $L$  and  $S$  combine to form the total angular momentum.



This scheme of coupling may be visualized in terms of a vector model of angular momentum.

$$J = L + S$$

➤ **Orbit-Orbit Interaction**

Consider orbital motion of two electrons,  $\ell_1$  and  $\ell_2$  are their quantum numbers,  $\ell_1 \hbar$  and  $\ell_2 \hbar$  are their angular momenta.  $\ell_1 \hbar$  and  $\ell_2 \hbar$  are quantized with respect to each other in such a way that they form resultant

$$L^* \text{ where } L^* = \frac{L(L+1)}{2} \hbar$$

$L=0, 1, 2, 3, 4, 5, 6, 7, \dots$  for S, P, D, F, G, H, I, J, ...

Consider an electron in the p orbit and other in the d orbit. Here two vectors  $\ell_1 = \sqrt{2}$  and  $\ell_2 = \sqrt{6}$  may orient themselves in any one of three positions  $L = \sqrt{2}, \sqrt{6}$  and  $\sqrt{12}$  corresponding to L=1, 2, 3 or P, D, F terms. All integral values of L from  $\ell_2 - \ell_1$  to  $\ell_2 + \ell_1$  are allowed.

➤ **Spin Spin Interaction**

With two electrons each having a spin angular momentum of  $s \cdot h/2\pi$  where  $s = [s(s+1)]^{1/2}$  and  $s=1/2$ . There are two ways in which a spin resultant  $S \cdot h/2\pi$  may be formed.

$s_1$  and  $s_2$  are spin quantum number of two electrons. This implies  $s_1 = (1/2)\sqrt{3}$  and  $s_2 = (1/2)\sqrt{3}$ . The two resultant quantum numbers are  $S=0$  and  $S=1$ .  $S=0$  gives rise to singlet and  $S=1$  to triplet.

Table 1 recapitulates the situation for an excited helium atom in the 1s 2p configuration. To derive the term symbols for the different spin-orbit states, we first need to calculate the total orbital angular momentum and total spin from those of the individual electrons, respectively. Then L and S are combined to find the total angular momentum of this group of electrons, J. The possible combinations for L, S and J are given as following:

$$L = |\ell_1 - \ell_2| \dots \ell_1 + \ell_2 \text{ (in integer steps)}$$

$$S = |s_1 - s_2| \dots s_1 + s_2 \text{ (in integer steps)}$$

$$J = |L - S| \dots L + S \text{ (in integer steps)}$$

<b>LS coupling</b>				
sub-shell	orbital	spin	total	term
1s	's' → $l_1 = 0$	$s_1 = \frac{1}{2}$		
2p	'p' → $l_2 = 1$	$s_2 = \frac{1}{2}$		
combi	$L =  l_1 - l_2 $ $= l_1 + l_2$ $= 1$	$S =  s_1 - s_2 $ $= 0$	$J =  L - S $ $= L + S = 1$	$^1P_1$
		$S = s_1 + s_2$ $= 1$	$J =  L - S  = 0$	$^3P_0$
			$J =  L - S  + 1 = 1$	$^3P_1$
			$J = L + S = 2$	$^3P_2$

Table 1

The term symbols are then composed by writing the total orbital angular momentum, L, in spectroscopic notation (S,P,D,F,... - capitalised, since this refers to the total orbital angular momentum of a group of electrons) with the total angular momentum J, as a subscript. Finally, the spin multiplicity,  $2S+1$ , is calculated from the total spin and attached to the term symbol as a leading superscript.

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The term symbols for all four terms in the 1s 2p configuration are shown in green in the table 1. In this case, there is a singlet state (1P1) and a triplet of states (3P03, 3P1, 3P2). The spin multiplicity indicates how many states there are in each group. In principle, any other electron configuration can be treated in exactly the same way, although the number of different terms can become quite large.

	sub-shell	orbital	spin
	2p	'p' → $l_1 = 1$	$s_1 = \frac{1}{2}$
	3p	'p' → $l_2 = 1$	$s_2 = \frac{1}{2}$
	combi	$L =  l_1 - l_2  = 0$	$S =  s_1 - s_2  = 0$
		$L =  l_1 - l_2  + 1 = 1$	$S = s_1 + s_2 = 1$
		$L = l_1 + l_2 = 2$	
$L \rightarrow$ $S \rightarrow$	0 → 'S'	1 → 'P'	2 → 'D'
0	$J =  L - S $ $= L + S$ $= 0 \rightarrow {}^1S_0$	$J =  L - S $ $= L + S$ $= 1 \rightarrow {}^1P_1$	$J =  L - S $ $= L + S$ $= 2 \rightarrow {}^1D_2$
1	$J =  L - S $ $= L + S$ $= 1 \rightarrow {}^3S_1$	$J =  L - S $ $= 0 \rightarrow {}^3P_0$	$J =  L - S $ $= 1 \rightarrow {}^3D_1$
		$J =  L - S  + 1$ $= 1 \rightarrow {}^3P_1$	$J =  L - S  + 1$ $= 2 \rightarrow {}^3D_2$
		$J = L + S$ $= 2 \rightarrow {}^3P_2$	$J = L + S$ $= 3 \rightarrow {}^3D_3$

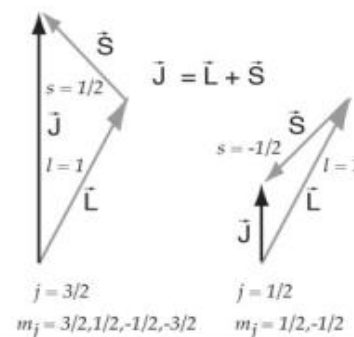
Table 2

Table 2 shows a simple example of a configuration with two valence electrons, 2p 3p. The total orbital angular momentum and the total spin are calculated from those of the individual electrons. In this case, three possible values for L rather than just one are obtained. Spin-wise, the situation is the same for any two-electron configuration since the spin of a single electron is always  $s=1/2$ . We then have to look at all possible permutations of the total orbital angular momenta and the total spin, as shown in the Table 2. For each permutation, we calculate the total angular momentum, J, and work out the term symbol as before. There are three separate singlets two proper triplets consisting of three states each, and one additional triplet state,  ${}^3S_1$ .

➤ **j-j Coupling**

For heavier atoms, another coupling scheme called j-j coupling provides better agreement with experiment.

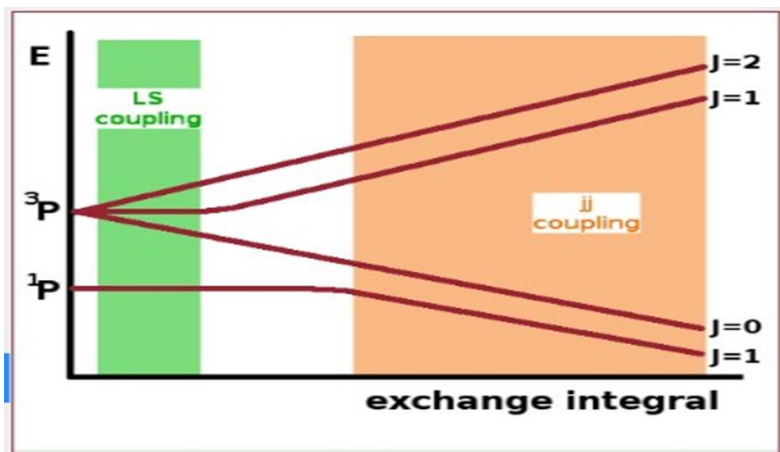
In j-j coupling, the orbital angular momentum  $\ell$ , and spin  $s$ , of each electron are first coupled to form a total angular momentum  $j$  for that electron. These single-electron total angular momenta are then combined into a total angular momentum J, for the group of electrons. This is in contrast to LS coupling, where the total orbital angular momentum L, and total spin S, of the system are calculated first and then combined to the total angular momentum, J, of the whole system.



$$J_1 = L_1 + S_1$$

$$J_2 = L_2 + S_2$$

$$J = \sum_i J_i$$



$j_1 \rightarrow$	$\frac{1}{2}$
$j_2 \rightarrow$	$\frac{1}{2}$
$\frac{1}{2}$	$J =  j_1 - j_2  \dots j_1 + j_2 = 0 \text{ or } 1$
$\frac{3}{2}$	$J =  j_1 - j_2  \dots j_1 + j_2 = 1 \text{ or } 2$

In general, the results from both coupling schemes are different. For example, for the 1s 2p configuration, jj coupling results in two doublets rather than a single and a triplet: For the 1s electron  $j_1 = |\ell - s_1| \dots |\ell + s_1| = 1/2$  and for the 2p electron  $j_2 = |\ell - s_2| \dots |\ell + s_2| = 1/2 \text{ or } 3/2$ . These combine as shown in the table 3, resulting in two doublets.

**Consider pd (palladium) electrons**

$s_1 = 1/2$	$\ell_1 = 1$		$s_2 = 1/2$	$\ell_2 = 2$
$J_1 = 1/2 \text{ or } 3/2$			$j_2 = 3/2 \text{ or } 5/2$	
Combining these four values in all possible ways				
$J_1 = 1/2, j_2 = 3/2$		$J = 1 \text{ and } 2$		
$J_1 = 3/2, j_2 = 3/2$		$J = 0, 1, 2$		

$j_1 = 1/2, j_2 = 5/2$

$J = 2, 3$

$j_1 = 3/2, j_2 = 5/2$

$J = 1, 2, 3, 4$

Energy states in terms of jj coupling for pd electrons will be

$(1/2, 3/2)_1 (1/2, 3/2)_2$

$(3/2, 3/2)_0 (3/2, 3/2)_1 (3/2, 3/2)_2 (3/2, 3/2)_3$

$(1/2, 5/2)_2 (1/2, 5/2)_3$

$(3/2, 5/2)_1 (3/2, 5/2)_2 (3/2, 5/2)_3 (3/2, 5/2)_4$

➤ **Ground state symbols for some selected (configurations) atoms and ions**

**1. Carbon,  $p^2$**

$$p^2 = +1, 0, -1 \quad 15\text{-(SP-1)A-TERM SYMBOLS}$$

$$2L = +1 + 0 = 1 \quad \text{Term} = \mathbf{P}$$

$$S = \frac{1}{2} + \frac{1}{2} = 1, \quad 2S+1=3$$

$$J = L+S, (L+S)-1, \dots, \dots, L-S = 2, 1, 0$$

The configuration is less than half filled. Hence, J must be minimum

$$J = 0 \text{ must be the ground state. The term symbol} = \mathbf{{}^3P_0}$$

**2. Nitrogen,  $p^3$**

$$p^3 = +1 \ 0 \ -1 \quad L = +1 + 0 + -1 = 0$$

$$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{3}{2}, \quad 2S + 1 = 4, \quad J = \frac{3}{2},$$

$$\text{Term} = \mathbf{{}^4S_{3/2}}$$

**3. Na,  $3s^1$  Na = [Ne]  $3s^1$**

$$L=0 \quad S = \frac{1}{2};$$

$$2S+1 = 2 \times \frac{1}{2} + 1 = 2$$

$$J = L + S \dots \text{to } L-S = \frac{1}{2}$$

$$\text{Term symbol for Na} = \mathbf{{}^2S_{1/2}}$$

**4.  $d^1$  - States**

$$m_l = 2 \ 1 \ 0 \ -1 \ -2 \quad L = 2$$

$$S = \frac{1}{2}, \quad 2S+1 = 2 \times \frac{1}{2} + 1 = 2$$

$$J = L+S \dots \dots \dots L-S = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$$

$$\text{Term symbol is } \mathbf{{}^2D_{3/2}}$$

**5.  $d^2$  - States ( $V3+$ )**

$$m_l = 2 \ 1 \ 0 \ -1 \ -2$$

$$L = 2+1 = 3$$

$$S = \frac{1}{2} + \frac{1}{2} = 1, \quad 2S+1 = 2(1) + 1 = 3$$

$$J = L+S; (L+S)-1; \dots \dots \dots L-S = 4, 3, 2 = L+S = 2$$

(Less than half filled) Term symbol is  $\mathbf{{}^3F_2}$

**6.  $d^3$  - States**

$$m_l = 2 \ 1 \ 0 \ -1 \ -2$$

$$L = 2 + 1 + 0 = 3$$

$$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{3}{2}, \quad 2S+1 = 2 \times \frac{3}{2} + 1 = 4$$

$$J = L+S \dots \dots \dots L-S = (3 + \frac{3}{2}) \dots \dots \dots \text{to } (3 - \frac{3}{2}) = \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2} \quad \text{Term}$$

$$\text{symbol for } d^3 \text{ is } \mathbf{{}^4F_{3/2}}$$

**7.  $d^4$  - States**

$$m_l = 2 \ 1 \ 0 \ -1 \ -2$$

$$L = 2 + 1 + 0 - 1 = 2$$

$$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = 2, \quad 2S+1 = 2 \times 2 + 1 = 5$$

$$J = L+S \text{ to } L-S = 4, 3$$

$$\text{Term symbol for } d^4 \text{ is } \mathbf{{}^5D_0}$$



**8.  $d^5$  - States**

$$ml = 2 \ 1 \ 0 \ -1 \ -2, \ L = 2 + 1 + 0 - 1 - 2 = 0$$

$$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = 5/2, \ 2S+1 = 2 \times 5/2 + 1 = 6;$$

$$J = (L+S), (L+S-1) \dots (L-S) = 5/2, 3/2, 1/2 = 5/2$$

( $J_{max}$ , Half filled- Highest)

Term symbol for  $d^5$  is  ${}^6S_{5/2}$

**9.  $d^8$  - States**

$$ml = 2 \ 1 \ 0 \ -1 \ -2 \ L = 2+1 = 3$$

$$S = \frac{1}{2} + \frac{1}{2} = 1; \ 2S+1 = 2(1) + 1 = 3$$

$$J = L+S \dots L-S = 3+1 \text{ to } 3-1 = 4, 3, 2$$

(more than half filled) Term symbol for  ${}^3F_4$

➤ **Microstates**

The number of microstates (N) of a system corresponds to the total number of distinct arrangements for “r” number of electrons to be placed in “n” number of possible orbital positions.

$$N = \text{No. of microstates}$$

$$= n! / (r!(n-r)!)$$

For a set of p orbitals  $n = 6$

Since there are 2 positions in each orbital Therefore,  $p^2$  ( $e = 2$  and  $n = 6$ ) so,  $N = 6! / (2!(6-2)!)$

$$= (6 \times 5 \times 4 \times 3 \times 2 \times 1) / ((2 \times 1) \times (4 \times 3 \times 2 \times 1))$$

$$= 15.$$

➤ **Derivation of microstates (Pegion Hole Diagram) :**

Russel Saunders coupling scheme gives all possible combinations of  $m_l$  and  $m_s$ , which collectively allowed and non-allowed. From all these spectral states, one should separate out allowed terms to determine the microstates present in the configuration. Thus this method becomes somewhat lengthy. Pegion Hole diagram method is another way to derive only the allowed spectral terms inclusive of all ground and excited states. From that one can determine the no. of microstates also for any configuration. The method is as discussed below example of  $P^2$ .

In this procedure

- 1) A table is prepared for all possible spin arrangements of electronic configuration to find out possible set of  $M_L$
- 2) From sets of  $M_L$ , L and term symbol can be obtained.
- 3) For derived terms J can be calculated to determine the microstates.

**(I) Pigion Hole Diagram For P<sub>2</sub> System**

■ Spin paired arrangement :

For two electrons, in spin paired arrangement  
 $S = \sum m_s = -\frac{1}{2} + \frac{1}{2} = 0$  ,  $2S + 1 = 1$  (singlet)

From spin arrangement table,

Set 1

$M_L = +2, +1, 0, -1, -2$

$M_L = 2L+1=5$

$L=2$  term is '**D**'

Thus term symbol is <sup>1</sup>D

Now  $J = L+S$  to  $L-S$

For given configuration,  $J = L = 2$

Term is <sup>1</sup>D<sub>2</sub>

Set 2

$M_L = 0$  ,  $2L + 1 = 1$  ,  $L = 0$  '**S**' term thus another allowed term is <sup>1</sup>S

$J = L + S$  to  $L - S$   $J = 0$

Thus spectral term is <sup>1</sup>S<sub>0</sub>

■ Spin unpaired 'arrangement

Set 1

$M_L = +1, 0, -1$

For two unpaired electrons,

$S = \sum m_s = \frac{1}{2} + \frac{1}{2} = 1$

$2S + 1 = 2(1) + 1 = 3$  (Triplet state)

$2L + 1 = 3$  ,  $L = 1$  , '**P**' term

Thus term symbol is <sup>3</sup>P

$J = L + S$  to  $L - S = 1 + 1$  to  $1 - 1 = 2, 1, 0$

terms are <sup>3</sup>P<sub>2</sub>, <sup>3</sup>P<sub>1</sub>, <sup>3</sup>P<sub>0</sub>,

Thus from pigion hole diagram, all possible allowed spectral term are <sup>1</sup>D<sub>2</sub>, <sup>3</sup>P<sub>2</sub>, <sup>3</sup>P<sub>1</sub>, <sup>3</sup>P<sub>0</sub>, <sup>1</sup>S<sub>0</sub> Microstates present in all these terms are 15 as follows.

<sup>1</sup>D<sub>2</sub> →  $(2S+1)(2L+1) = (1)(5) = 5$

<sup>3</sup>P<sub>2</sub> →  $(2S+1)(2L+1) = (3)(3) = 9$

<sup>1</sup>S<sub>0</sub> →  $(2S+1)(2L+1) = (1)(1) = 1$

total 15 microstates

For,

<sup>1</sup>D<sub>2</sub>,  $J = 2, M_J = 5$

<sup>3</sup>P<sub>2</sub>,  $J = 2, M_J = 5$

<sup>3</sup>P<sub>1</sub>,  $J = 1, M_J = 3$

<sup>3</sup>P<sub>0</sub>,  $J = 0, M_J = 1$

<b>m<sub>l</sub></b>						
<b>+1</b>	↑		↑	↓↑		
<b>0</b>	↓	↑			↓↑	
<b>-1</b>		↓	↓			↓↑
<b>M<sub>L</sub></b>	<b>+1</b>	<b>-1</b>	<b>0</b>	<b>+2</b>	<b>0</b>	<b>-2</b>

<b>m<sub>l</sub></b>			
<b>+1</b>	↑	↑	
<b>0</b>	↑		↑
<b>-1</b>		↑	↑
<b>M<sub>L</sub></b>	<b>+1</b>	<b>0</b>	<b>-1</b>



$^3S_0, J = 0, M_J = 1$

total 15 microstates

Like this configuration, allowed term for  $^1P$  system can be determined to calculate microstates of  $^1P$  using pegion hole diagram.

### (II) Pegion Hole diagram for d2 configuration

d2 configuration also possess two electrons and two electrons may arrange their spin either paired or unpaired. So triplet (S=1) and singlet (S=0) terms are possible which can be derived as follows by pegion hole diagram.

#### ■ Spin Paired arrangement (S=0)

<b><math>m_l</math></b>															
<b>+2</b>	↑↓					↑	↑	↑	↑						
<b>+1</b>		↑↓				↑				↑	↑	↑			
<b>0</b>			↑↓				↓			↓			↑	↑	
<b>-1</b>				↑↓				↓			↓		↓		↑
<b>-2</b>					↑↓				↓			↓		↓	↑
<b><math>M_L</math></b>	<b>+4</b>	<b>+2</b>	<b>0</b>	<b>-2</b>	<b>-4</b>	<b>+3</b>	<b>+2</b>	<b>+1</b>	<b>0</b>	<b>+1</b>	<b>0</b>	<b>-1</b>	<b>-1</b>	<b>-2</b>	<b>-3</b>

From table;

Set-1

$$M_L = +4, +3, +2, +1, 0, -1, -2, -3, -4$$

$$M_L = 2L + 1 = 9 \quad L = 4 \text{ 'G' term}$$

$$S = 0 \text{ spin multiplicity} = 2S + 1 = 1.$$

Thus term symbol is  $^1G$

Set-2

$$M_L = +2, +1, 0, -1, -2$$

$$M_L = 2L + 1 = -5 \quad L = 2 \text{ 'D' term}$$

Thus term symbol is  $^1D$

Set-3

$$M_L = 0, \quad 2L + 1 = 1 \text{ thus } L = 0 \text{ Thus term symbol is } ^1S.$$

#### ■ Spin unpaired arrangement (S = 0)

<b><math>m_l</math></b>															
<b>+2</b>	↑	↑	↑	↑											
<b>+1</b>	↑					↑	↑	↑							
<b>0</b>		↑				↑			↑	↑					
<b>-1</b>			↑				↑		↑			↑		↑	
<b>-2</b>					↑			↑		↑		↑			
<b><math>M_L</math></b>	<b>+3</b>	<b>+2</b>	<b>+1</b>	<b>0</b>	<b>+1</b>	<b>0</b>	<b>-1</b>	<b>-1</b>	<b>-2</b>	<b>-3</b>					

From spin arrangement table

Set 1

$$M_L = +3, +2, +1, 0, -1, -1, -2, -3$$

$$M_L = 2L + 1 = 7, L = 3 \quad \text{'F' term}$$

Thus term symbol is  ${}^3\mathbf{F}$

Set 2

$$M_L = +1, (-1)$$

$$M_L = 2L + 1 = 3, L = 1 \quad \text{'P' term}$$

Thus term symbol is  ${}^3\mathbf{P}$

All these arrangements of paired and unpaired spin gives only allowed terms for  $d^2$  configuration and their order of energy is  ${}^3\mathbf{F} < {}^3\mathbf{P} < {}^1\mathbf{G} < {}^1\mathbf{D} < {}^1\mathbf{S}$  and the order of their stability is  ${}^3\mathbf{F} > {}^3\mathbf{P} > {}^1\mathbf{G} > {}^1\mathbf{D} > {}^1\mathbf{S}$ .

➤ **Questionary**

**One mark questions**

- 1) Which quantum number is related with the orientation of orbitals?
- 2) What is the use of coupling scheme?
- 3) What is resultant spin quantum number?
- 4) What is spin multiplicity?
- 5) What is spin multiplicity for  $S = 2$ ?
- 6) For P2 electrons, what is L value?
- 7) What is orbital multiplicity?
- 8) What is orbital multiplicity for  $L = 2$ ?
- 9) What is another name of L S coupling scheme?
- 10) Which value is derived by L — S coupling?
- 11) What is the symbol of spectroscopic state?
- 12) For IS state, what is J value?
- 13) For d2 system, what will be spin multiplicity?
- 14) What is L-value for  ${}^3F$  state?
- 15) For P2 system, what is the order of energy of  ${}^1D$ ,  ${}^3P$  and  ${}^1S$ ?
- 16) What is the range of J and j values?
- 17) Give equation to calculate microstates.
- 18) In  ${}^3F_2$  How many microstates are available.
- 19) For  $S = 1$  and  $L = 2$ , how many microstates are available?
- 20) Give any one rule given by Hund for the determination of ground state term symbol

**Answer the following questions in short**

- 21) Define following terms.  
(i) Spectral term symbol, (ii) Spin multiplicity, (ii) Orbital multiplicity  
(iv) Microstates
- 22) Calculate  $S$ ,  $M_S$ ,  $L$ ,  $M_L$ ,  $J$  and  $M_J$  for following terms,  
(i)  ${}^3F$  (ii)  ${}^5D$  (iii)  ${}^1S$  (iv)  ${}^4F$  (v)  ${}^1G$
- 23) Derive ground state spectral term or Derive Russell-Saunders term  
(i)  $Cu^{+2}$  (ii)  $Ti^{+3}$   
(iii)  $Ni^{+2}$  (iv)  $Mn^{+2}$  (v)  $Fe^{+2}$  (vi)  $d^2$  (vii)  $d^3$   
(viii)  $d^4$  (ix)  $d^7$

**Answer the following questions in short [2 Marks]**

- 24) Calculate microstates for  
(i)  $Cr^{+3}$   
(ii)  $Mn^{+5}$   
(iii)  $Fe^{+3}$   
(iv)  $d^1$   
(v)  $d^2$

**Answer the following questions: [3 Marks]**

- 25) Write a short note.  
(i) s-s coupling (ii) l-l coupling (iii) l-s coupling (iv) Microstate  
**Answer the following questions in detail : [5 Marks]**
- 26) Discuss Russell-Saunders coupling scheme.
- 27) Discuss l-l coupling in  $P^3$  system with vector representation.
- 28) Derive all possible spectral states for  $P^2$  system and arrange them in order of energy.
- 29) Discuss Hund rules for the determination of ground state term symbol.
- 30) Derive allowed spectral terms for  $d^2$  system using peqion hole diagarn and arrange them in order of stability.
- 31) Derive all possible spectral terms for  $d^2$  using vector diagram and allowed terms using Hand's rule.