

**Title: Term Symbols**

**Course: M.Sc(Chemistry) Semester 1**

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## ❖ TERM SYMBOLS

\* Although the quantum numbers and energies of individual electrons can be described in fairly simple terms, interactions between electrons complicate this picture. As a result of repulsions between electrons, electrons tend to occupy separate orbitals, and as a result of exchange energy, electrons in separate orbitals tend to have parallel spins.

\*Consider, for example the energy levels, of a carbon atom. Carbon has the electron configuration  $1s^2 2s^2 2p^2$ . At first, we might expect the  $p$  electrons to be degenerate, and have the same energy. However, there are three major energy levels for the  $p^2$  electrons, differing in energy by **pairing** and **exchange** energies. In addition, the lowest major energy level is split into three slightly different energies, for a total of five energy levels. Each energy level can be described as a combination of the  $ml$  and  $ms$  values of the  $2p$  electrons. *Independently*, each of the  $2p$  electrons could have any of six possible  $ml, ms$  combinations:

$n = 2, l = 1$	(quantum numbers defining $2p$ orbitals)
$ml = +1, 0, \text{ or } -1$	(three possible values)
$ms = +1/2 \text{ or } -1/2$	(two possible values)

\*The  $2p$  electrons are not independent of each other, however; the orbital angular momenta (characterized by  $ml$  values) and the spin angular momenta (characterized by  $ms$  values) of the  $2p$  electrons interact in a manner called **Russell–Saunders coupling** or **LS coupling**. An oversimplified view is to consider an electron as a particle; its orbital motion and spin generate magnetic fields (a charge in motion generates a magnetic field) and these fields created by multiple electrons can interact. These interactions produce atomic states called **microstates** that can be described by new quantum numbers:

$ML = \sum m_l$	Total orbital angular momentum
$MS = \sum m_s$	Total spin angular momentum

\*Because the quantum numbers  $m_l$  and  $m_s$  provide information about the magnetic fields generated by electrons due to their orbital and spin, respectively, we need to determine how many possible combinations of  $m_l$  and  $m_s$  values there are for a  $p^2$  configuration to assess the different possible interactions between these fields.

\*\* These combinations allow determination of the corresponding values of  $ML$  and  $MS$ . For shorthand, we will designate the  $m_s$  value of each electron by a superscript +, representing  $m_s = +1/2$ , or  $-1/2$ , representing  $m_s = -1/2$ . For example, an electron having  $m_l = +1$  and  $m_s = +1/2$  will be written as  $1+$ .

$$\text{orbital angular momentum} = \left[ \sqrt{l(l+1)} \right] \frac{h}{2\pi}$$

\*We assume that the energy of a multi-electron species and its orbital angular momentum is determined by a resultant orbital quantum number,  $L$ , which is obtained directly from the values of  $l$  for the individual electrons.

### Russell-Saunders Symbols

\* An atom's electronic state depends entirely on its unfilled sub shells. Because electrons distribute themselves in a symmetric manner, the inner shell electrons end up canceling out each other's momenta.

\* For an atom in the configuration  $1s^2 2s^2 p^2$ , only the two p-electrons matter. For an atom in the configuration  $1s^2 2s^1 2p^1$ , we have to examine the 2s and 2p electrons. Atoms have quantum numbers that are directly analogous to the electronic quantum numbers.

### ❖ The Total Orbital Angular Momentum Quantum Number: $L$

\* One might naively think that you could get the total angular momentum of an atom by simply adding up the  $l$  values of the individual electrons. The problem with this idea is that the angular momenta of the various electrons are not necessarily pointing in the same direction. If two electrons are revolving in the same direction as each other, you would add their  $l$  values. If they were revolving opposite to each other, you would subtract them.

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

**Example:** What are the possible  $L$  values for the electrons in the  $1s^2 2s^2 2p^2$  configuration of carbon?

**Solution:-** Both open-shell electrons (i.e., the  $2p$  electrons) are  $l=1$ . The possible combinations are **2, 1, 0**.

\* **Example :** What are the possible  $L$  values for the electrons in the  $[Xe] 6s^2 4f^5 5d^1$  ?

**Solution:-** We have an  $l=3$  and an  $l=2$  electron.

$3+2=5$  and  $3-2=1$ . The possible combinations are **5, 4, 3, 2, 1**

### ❖ The Total Magnetic Quantum Number: $M_l$

\*  $L$  told you how much angular momentum there was,  $M_l$  tells you which direction it is pointing. Like  $L$ , a given configuration can have several possible values of  $M_l$ , depending on the electrons' relative orientation. Unlike  $L$ ,  $M_l$  is allowed to have negative values. To list the possible  $M_l$  values for a two electron system, take the case where both  $m_l$  are **positive**, then take the case where they are both **negative**, and then fill in the numbers in between.

$$Ml = ml_1 + ml_2, ml_1 + ml_2 - 1, \dots, -ml_1 - ml_2$$

**\*Example :-** What are the possible values  $Ml$  of a zirconium atom with the  $[Kr] 5s^2 4d^2$  electron configuration?

**Solution:** Both open-shell electrons (i.e., the  $4d$  electrons) are  $l=2$

, so the values are **4, 3, 2, 1, 0, -1, -2, -3, -4.**

### ❖ The Total Spin Magnetic Quantum Number: $M_s$

\* It is easily computed by finding all of the possible combinations of  $m_s$ . since  $m_s$  for each individual electron can only be  $+1/2$  or  $-1/2$ , this isn't too complicated.

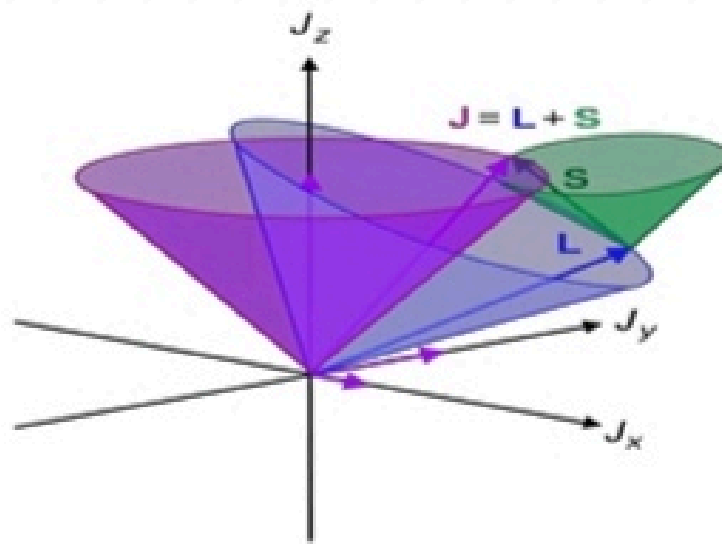
$$M_s = ms_1 + ms_2, ms_1 + ms_2 - 1, \dots, ms_1 - ms_2$$

Ex:- What are the  $M_s$  values for  $1s^2 2s^2 2p^2$  ?

**Solution  $M_s=1,0,-1$**

### ❖ The Total Angular Momentum Quantum Number $J$

\* The total orbital angular momentum of an atom (measured in terms of  $L$ ), and the total spin angular momentum of an atom (measure in  $S$ ) combine to form total angular momentum, a number that is quantized by the number  $J$ .  $L$  and do not necessarily have to be pointing in the same direction (Figure below), so  $J$  can range from  $L+S$  to  $|L-S|$ .



***L-S coupling.*** Total angular momentum  $J$  is **purple**, orbital  $L$  is **blue**, and spin  $S$  is **green**.

For light atoms, the spin-orbit interaction (or coupling) is small so that the total orbital angular momentum  $L$  and total spin  $S$  are good quantum numbers. The interaction between  $L$  and  $S$  is known as *LS coupling*, *Russell-Saunders coupling*, or *Spin-Orbit coupling*. Atomic states are then well described by term symbols of the form

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

Where;

$S$  is the total spin quantum number.  $2S + 1$  is the spin multiplicity, which represents the number of possible states of  $J$  for a given  $L$  and  $S$ , provided that  $L \geq S$ . (If  $L < S$ , the maximum number of possible  $J$  is  $2L+1$ ). This is easily proved by using,  $J_{max} = L+S$  and  $J_{min} = |L - S|$ , so that the number of possible  $J$  with given  $L$  and  $S$  is simply  $J_{max} - J_{min} + 1$  as  $J$  varies in unit steps.

$J$  is the total angular momentum quantum number.

$L$  is the total orbital quantum number in spectroscopic notation. The symbols of  $L$  are:

$$L = 0 \ 1 \ 2 \ 3 \ 4 \ 5 \ 6 \ 7 \ 8 \ 9 \ 10 \ 11 \ 12 \ 13$$

$$S \ P \ D \ F \ G \ H \ I \ K \ L \ M \ N \ O \ Q \ R$$