

Quantum numbers associated with the vector atom model.

1. The Principal quantum number (n).

This is identical with the one used in Bohr-Sommerfeld theory. The serial number of the shells starting from the innermost is designated as its principal quantum number (n). It can take only integral values excluding zero i.e.

$$n = 1, 2, 3, \dots$$

2. The orbital quantum number (l).

This may take any integral value $0, 1, 2, 3, \dots, (n-1)$. Thus if $n = 4$, then l can take four values $0, 1, 2, 3$.

By convention an electron for which

$l = 0$, is called s electron

$l = 1$ is called p electron

$l = 2$ f electron

$l = 3$ d electron

The orbital angular momentum p_l of the electron is given by $p_l = l\hbar$.

According to wave mechanics $p_l = l(l+1)^{1/2}\hbar$.

3. The spin quantum number (s).

This has only one value $s = 1/2$.

The spin angular momentum $p_s = +s\hbar$.

where $s = 1/2$ According to wave mechanics we have $p_s = s(s+1)^{1/2}\hbar$.

4. Total angular momentum quantum number (j).

(11)

It represents the total angular momentum of the electron which is the sum of the orbital angular momentum of the electron and spin angular momentum.

The vector \vec{j} is defined by the equation $\vec{j} = \vec{l} + \vec{s}$ with the restriction of \vec{j} is

positive. The spin angular momentum

$s = \pm 1/2$ $\therefore j = l \pm s$ plus sign when

s is parallel to l and minus when

s is antiparallel to l .

Thus for $l = 2$ and

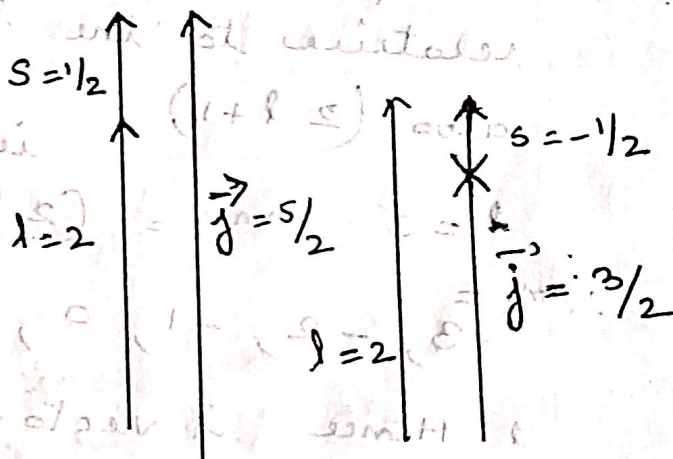
$$s = 1/2$$

$$j = 2 + 1/2 = 5/2$$

IIIrd for $l = 2$ and

$$s = -1/2$$

$$j = 2 - 1/2 = 3/2$$



Total angular momentum of the electron

$= p_j = j h$ according to wave mechanics.

$$p_j = \sqrt{j(j+1)} h$$

To explain the splitting of spectral lines in a magnetic field, three more magnetic quantum numbers are introduced.

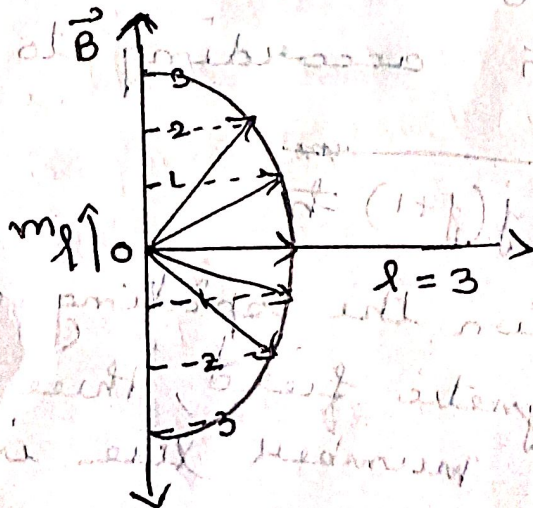
5. Magnetic orbital quantum number (m_l)

The projection of orbital quantum number l on the magnetic field direction is called the magnetic orbital quantum number m_l . The possible values of m_l are $l, l-1, l-2, \dots, 0, \dots, -1, -2, -3, \dots, -l$ i.e. there are $(2l+1)$ possible values of m_l .

For example when $l=3$, the angle θ b/w l and B is given by $\cos \theta = \frac{m_l}{l}$. Conversely, the permitted orientations of the l vector relative to the field direction B is

also $(2l+1)$ i.e. $+3$ to -3 & 0 of $l=3$.
 $l=3$ $m_l = (2l+1) = (6+1) = 7$ values.

$m_l = -3, -2, -1, 0, 1, 2, 3$ respectively.
 Hence l vector can have only seven directions. l cannot be inclined to B at any other angle. This is known as spatial quantisation.



6. Magnetic spin quantum number (m_s)

This is the projection of spin vector s along the direction of the magnetic field. The spin angular momentum (s) can assume only two possible positions with respect to the magnetic field. It may be parallel to it or antiparallel. m_s can have only two values $+1/2$ and $-1/2$.

Fig (a)

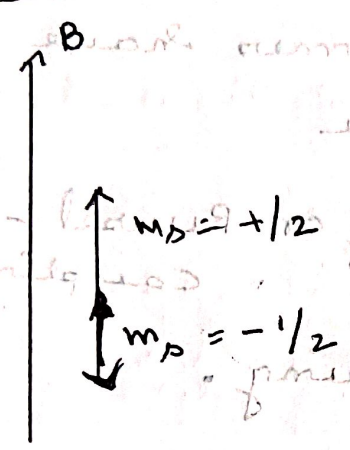


Fig (a)

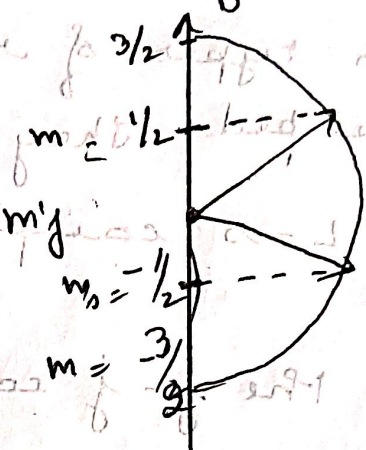


Fig (b)

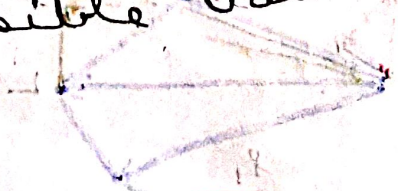
4. Magnetic total angular momentum quantum number (m_j)

This is the projection of total angular momentum vector j on the direction of the magnetic field. Since we are dealing with single electron j can have only odd half integral values ($j = l \pm 1/2$).

Hence m_j must have only odd half integral values. m_j can have only $(2j+1)$ values. From $+j$ to $-j$. Zero excluded.

Fig (b) shows possible values of m_j

for $j = 3/2$



Coupling schemes

In an atom having two or more electrons, the orbital and spin angular momenta of all its electrons can be added together in two ways. The method of combination depends on the interaction or coupling between the orbital and spin angular momenta.

Two types of schemes have been developed. They are

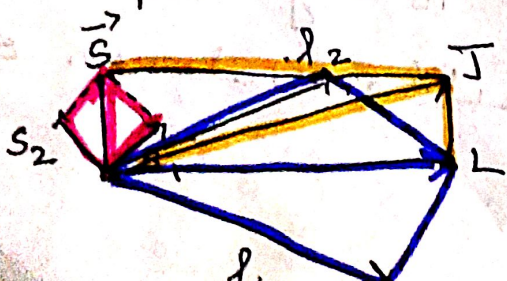
- (1) L-s coupling or Russell-Saunders coupling
- (2) The j-j coupling.

1) L-s coupling

This type of coupling which occurs most frequently is the L-s coupling. In this type, all the orbital angular momentum vectors of various electrons combine to form L and independently, all their spin angular momentum vectors combine to form S. The resultant L and resultant S combine to form the total angular momentum J. of the atom.

$$L = \sum l_i \quad S = \sum s_i$$

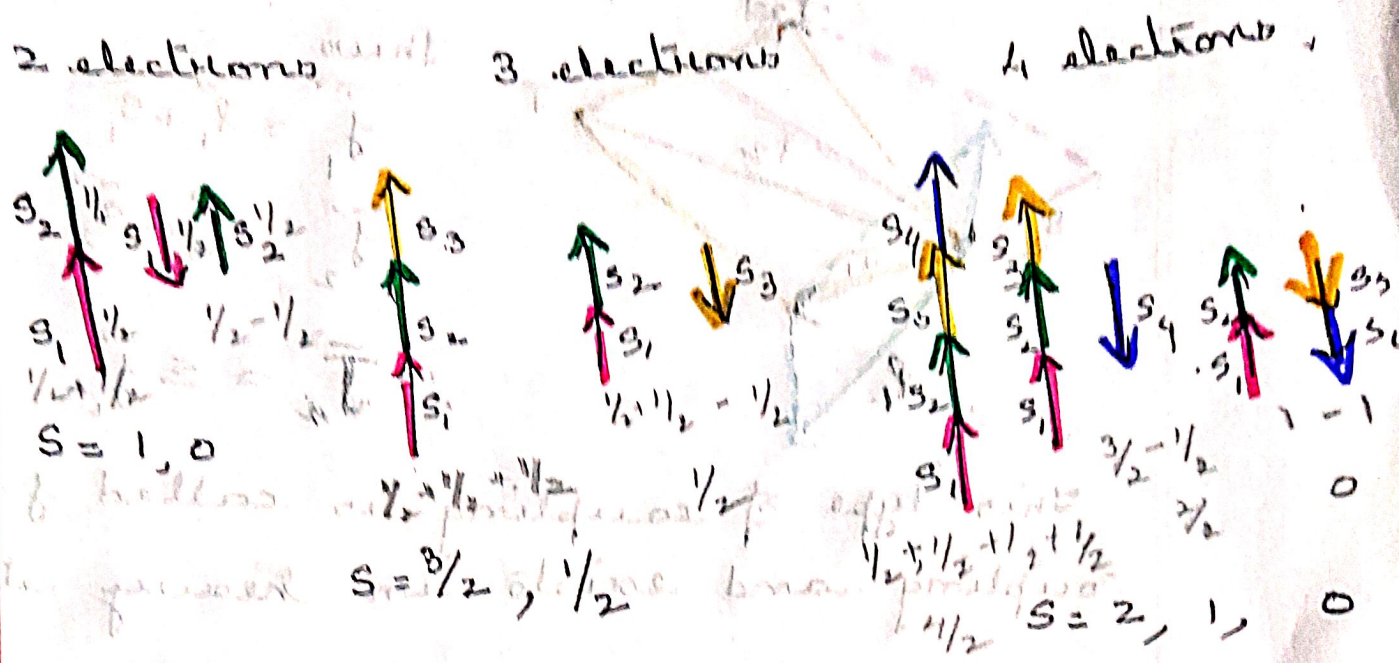
$$J = L + S$$



L is always integer included zero.

S is an integer for an even

even number of electrons and odd multiple of $\frac{1}{2}$ for odd number of electrons.



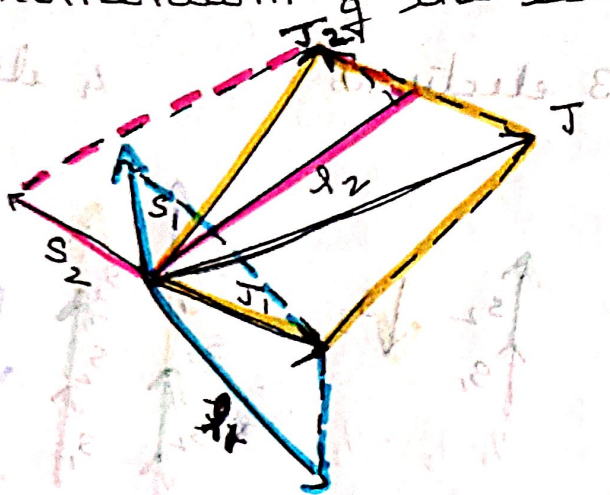
Hence J must be an integer, if S is an integer and J must be an odd multiple of $\frac{1}{2}$ if S is an odd multiple of $\frac{1}{2}$.

It can be shown that, when $L > S$, J can have $(2S+1)$ values and when $L < S$ J can have $(2L+1)$ values. In particular if $L = 0$ J can have only one value namely $J = S$.

2. J. J coupling:

This method is employed when the interaction between the spin and orbital vectors of each electron is stronger than the interaction between either the spin vectors or the orbital vectors of the different electrons. The orbital and spin angular

momenta of each electron in the atom are added to obtain the resultant angular momentum of the electron



Thus

$$\vec{j}_1 = \vec{l}_1 + \vec{s}_1$$

$$\vec{j}_2 = \vec{l}_2 + \vec{s}_2$$

$$\therefore \vec{J}_e = \sum \vec{j}_e$$

This type of coupling is called $j-j$ coupling and exists in heavy atoms

Application of spatial quantisation

The resultant vectors L , S and J representing the atom, can be obtained by the above coupling schemes. According to quantum theory L , S and J are quantised in magnitude and direction. Hence the number of permitted orientation of L , S , and J with respect to a given field direction are $(2L+1)$, $(2S+1)$ and $(2J+1)$ respectively, the corresponding magnetic quantum numbers $m_L = \sum m_l$, $m_S = \sum m_s$ and $m_J = \sum m_j$ can have only

$(2L+1)$, $(2S+1)$ and $(2J+1)$ values respectively