Atomic spectra

Sommerfeld̓s model:

Sommerfeld succeeded partially in explaining fine structure for atomic spectra by extending Bohr theory as follows :

i) He allowed the possibility of elliptical orbits for the electrons in addition to Bohr circular orbit.

ii) He took note of the relativistic variation of electron mass with velocity which was different at different parts of the elliptical orbit.

Now, when elliptical orbits are permitted, one has to deal with two variable quantities. In polar coordinates, these are :

i) The varying distance of the electron from the nucleus i.e. r.

ii) The varying angular position of the electron with respect to the nucleus i.e. the azimuthally angle φ.

To deal with these two variables, we need two quantum numbers :

i) One is the original quantum number n of Bohr's theory.

ii) The other is new quantum number called orbital quantum number which has introduced to characterize the angular momentum of an orbit i.e. it determines the orbital angular momentum of the electron which its value varies from zero to (n-1) in steps of unity. So : $l = 0 \rightarrow (n-1)$.

This orbital is useful in finding the possible as the Eq:

$$\frac{b}{a} = \frac{l+1}{n} \qquad \text{----------------(18)}$$

If $a=b \rightarrow$ circular but if $a \neq b \rightarrow$ elliptical.

For every principle quantum number n there is n possible orbits called sub orbits or sub shell i.e :

n=1 1 sub shell

n=2 2 sub shell

n=3 3 sub shell

For example :

n=4 l=0,1,2,3

It is common to assign letters to l values as given below :

Orbital quantum number l : 0 1 2 3 4 5

Electron designator : s p d f g h

The maximum number of electrons allowed in any sub shell is : 2(2l+1).

	K	L	M	N
Principle quantum number n	1	2	3	4
Orbital quantum number l	0	0 1	0 1 2	0 1 2 3
Possible electrons	1s	2s 2p	3s 3p 3d	4s 4p 4d 4f
Maximum number of Electron= 2(2l+1)	2	2 6	2 6 10	2 6 10 14
Total number of electrons=$2n^2$	2	8	18	32

Orbital Magnetic QuantumNumber(m_l):

This number arises out of the fact that an electron in an orbit constitutes a rotating charge and hence electric current which has its associated magnetic field and magnetic moment.

It means that m_l can have one of the (l +1) values ranging from $-l$ to $+l$ including zero. i.e. $l,(l-1),(l-2),(l-3),\ldots\ldots 1,\ 0,\ -1\ ,-2\ ,\ldots\ldots (l-2)\ ,(l-1),\ -l$. these values corresponds to various sub shells in which electrons rotate around the nucleus.

Magnetic Spin QuantumNumber(m_s):

It is the numerical value of the projection of the spin vector(s) on the field direction. This spin vector is capable of orientation only in either of the two ways:

parallel or anti-parallel to the surrounding field. Hence, m_S can have only two values +1/2 or -1/2.

Different shells, sub shells and sub-subshells:

n shell	l sub shell	m_l sub- sub shell
1	0	0
2	0	0
2	1	+1 0 -1

3	0	0
	1	1 0 -1
	2	+2 +1 0 -1 -2

Total AngularQuantum Number :

It has found that coupling occurs between the spin and orbital angular momenta of an electron which been described by another quantum number j called the **Total angular quantum number**, the value of j : $j=l+s$, $j=l-s$

With the restriction that j must be positive.

Magnetic Quantum Number(m_j) :

This quantum number comes into existence because of space quantization of the total angular momentum P_j. it is quantized component of j with respect to the direction of the applied external magnetic field. The quantum number m_j can have only (2j+1) values ranging from –j to +j with zero excluded.

Example :

If j=5/2 , then allowed orientation are :

m_j = 5/2,3/2,1/2,-1/2,-3/2,-5/2.

Values of n, l, j, m_j Quantum Numbers:

The values of different quantum numbers for electrons occupying different shells and sub shells, are as undertake n=1 then l=0 , j=l+s=0+1/2=1/2 and j=l-s=0-1/2=-1/2 must be neglected

mj=1/2,-1/2

n	l	j	m_j
1	0	1/2	1/2
1	0	1/2	-1/2

Example:

Take n=2 l=0,1 s=1/2

If l=0 , j=0+1/2=1/2 , m_j =1/2,-1/2

If l=1 , j=1+1/2=3/2 or j=1-1/2=1/2 **So** m_j=3/2,1/2,-1/2,-3/2 and m_j=1/2,-1/2 , Therefore :

n	l	j	m_j
2	0	1/2	1/2
2	0	1/2	-1/2
2	1	3/2	3/2
2	1	3/2	1/2
2	1	3/2	-1/2
2	1	3/2	-3/2
2	1	1/2	1/2
2	1	1/2	-1/2

Four quantum numbers neglecting spin –orbit interaction:

If we neglect the spin orbit interaction, then the state of an electron in an atom can be completely specified by the following four quantum numbers:

1) Principle quantum number (n).
2) Orbital quantum number (l).
3) Orbital magnetic quantum number (m_l).
4) Magnetic spin quantum number (m_s).

Pauli's Exclusion Principle:

It states that in one atom, no two electrons can have the same set of values for the four quantum numbers n, l, m_l ,m_s. or (n, l, j, mj).

Example :

What is the maximum number of the electrons in an atom that can share the following quantum numbers?

i) n, l ,m_l,m_s ii) n, l,m_l iii) l iv) n ?

Example :

How are electrons distributed in the various sub shell for n=3, give the quantum numbers in the first sub shell.

Example:

Find the number of electrons in atoms which have the following level filled in the ground state

a) K and L shells , the 3s sub shell and one half of the 3p sub shell.
b) The K,L,M shells and the 4s,4p and 4d sub shells.

Quantum Mechanic and the Quantum Numbers:

The orbital quantum number l determines the variation of the wave function of the electron as the angle θ changed. Also from quantum mechanics, the magnitude of the angular momentum L of the electron in the atom is given by:

$$L = \sqrt{l(l+1)}\,\hbar \qquad \text{-----------(19)}$$

The z-component of the angular momentum L of the electron in the atom I given by:

$$L_z = m_j\hbar \qquad \text{--------------(20)}$$

The angle θ which the vector L rotating around is:

$$\cos\theta = \frac{L_z}{L} = \frac{m_j\hbar}{\sqrt{l(l+1)}\,\hbar} = \frac{m_j}{\sqrt{l(l+1)}} \qquad \text{--------(21)}$$

$$S = s\hbar = \frac{1}{2}\,\hbar \qquad \text{-----------(22)}$$

Where s is the Spin Quantum Number. It can take only the one value 1/2 . As quantum mechanics developed, scientist found that the correct magnitude of S is not 1/2 ħ but is given by:

$$S = \sqrt{s(s+1}\hbar = \frac{3}{2}\,\hbar \qquad \text{--------(23)}$$

$S_z = m_s\hbar =$, $m_s = 1/2$ or $-1/2$ --------(24)

and m_S is called the spin magnitude quantum number.

Total Angular Momentum Vector J :

$$J = L+s \qquad \text{---------}(24)$$

$$J = \sqrt{j(j+1)}\,\hbar \qquad \text{-----------}(25)$$

The magnitudes of the angular momentum L,S,J in units of ħ according to quantum mechanics , are given by:

$$\frac{L}{\hbar} = \sqrt{l(l+1)}\,, \quad \frac{S}{\hbar} = \sqrt{s(s+1)}\,, \quad \frac{J}{\hbar} = \sqrt{j(j+1)} \qquad \text{--------}(26)$$

$$\cos\theta = \frac{j(j+1)-l(l+1)-s(s+1)}{\sqrt{l(l+1)}\sqrt{s(s+1)}} \qquad \text{-----------}(27)$$

Example:

Calculate the two possible orientation of the spin vector S with respect to a magnetic field direction.

Example:

Consider a d electron in a one electron atomic system. Calculate the value of

a. l, s, j
b. L,S,J
c. Possible angles between L and S.