Structure of Atom

Quantum Mechanical Model of Atom

Classical mechanics, based on Newton's laws of motion, successfully describes the motion of all macroscopic objects. It fails when applied to microscopic objects like electrons, atoms, molecules etc. This mainly because of the fact that classical mechanics ignores the concept of dual behavior of matter. The branch of science that takes into account this dual behavior of matter is called quantum mechanics. (Wave & particle)

Quantum mechanics is a theoretical science that deals with the study of the motions of the microscopic objects that have both observable wave like and particle like properties.

Orbitals and Quantum Numbers

A large number of orbitals are possible in an atom. Qualitatively these orbitals can be distinguished by their size, shape and orientation. An orbital of smaller size means there is more chance of finding the electron near the nucleus. Similarly shape and orientation mean that there is more probability of finding the electron along certain directions than along others. Atomic orbitals are precisely distinguished by what are known as quantum numbers. Each orbital is designated by three quantum numbers labeled as n, l and m_1.

The principal quantum number 'n' is a positive integer with value of n = 1,2,3…… The principal quantum number determines the size and to large extent the energy of the orbital. For hydrogen atom and hydrogen like species (He^+, Li^{2+},…… etc.) energy and size of the orbital depends only on 'n'.

The principal quantum number also identifies the **shell.** With the increase in the value of 'n', the number of allowed orbital increases and **are given by 'n^2' All the orbitals of a given value of 'n' constitute a single shell of atom** and are represented by the following letters

n = 1 2 3 4 …………………

Shell = K L M N ……………………

Size of an orbital increases with increase of principal quantum number ‘n’. In other words the electron will be located away from the nucleus. Since energy is required in shifting away the negatively charged electron from the positively charged nucleus, the energy of the orbital will increase with increase of n.

Azimuthal quantum number. ‘l’ is also known as **orbital angular momentum or subsidiary quantum number.** It defines the three-dimensional shape of the orbital. For a given value of n, l can have n value of n, the possible value of l are : l = 0, 1, 2, ……. (n – 1)

For example, when n = 1, value of *l,* value of l is only 0. For n = 2, the possible value of l can be 0 and 1. For n = 3, the possible l values are 0, 1 and 2.

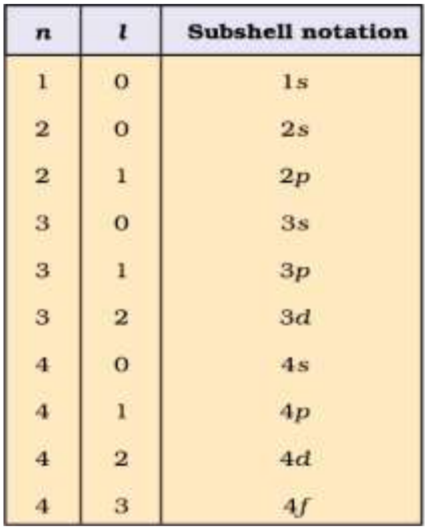
Each shell consists of one or more **sub-shells** or **sub-levels.** The number or sub-shells in a principal shell is equal to the value of n. For example in the first shall (n=1), there is only one sub-shell which corresponds to l=0. There are two sub-shells (l=0, 1) in the second shell (n=2), three (l=0, 1, 2) in third shell (n=3) and so on. Each sub-shell is assigned an azimuthal quantum number (l). Sub-shells corresponding to different values of l are represented by the following symbols.

Value for l : 0 1 2 3 4 5 ……………..

Notation for s p d f g h ………………

Table shows the permissible values of ‘l’ for a given principal quantum number and the corresponding sub-shell notation.

Sub-shell Notations



n	l	Subshell notation
1	0	1s
2	0	2s
2	1	2p
3	0	3s
3	1	3p
3	2	3d
4	0	4s
4	1	4p
4	2	4d
4	3	4f

Magnetic orbital quantum number. 'm_1' gives information about **the spatial orientation of the orbital with respect to standard set of co-ordinate axis.** For any **sub-shell (defined by 'l' value)** 2l+1 values of m_1 are possible and these values are given by:

m_1 = -l,-(l – l), - (l – 2)….. 0,1…. (l – 2), (l – 1), l

Thus for l = 0, the only permitted value of m_1 = 0, [2(0)+1 = 1, one s orbital. For l = 1, m_1 can be – 1, 0 and +1 [2(1)+1 = 3, three p orbitals]. For l = 2, m_1 = -2, -1, 0, +1 and +2, [2(2)+1 = 5, five d orbitals]. It should be noted that the values of m_1 are derived from l and that the value of l are derived from n.

Each orbital in an atom, therefore, is defined by a set of values for n, l and m_1. An orbital described by the quantum numbers n = 2, l = 1, m_1 = 0 is an orbital in the p sub-shell of the second shell. The following chart gives the relation between the sub-shell and the number of orbitals associated with it.

Value of l	0	1	2	3	4	5
Sub-shell notation	s	p	d	f	g	h
Number of orbitals	1	3	5	7	9	11

Electron spin 's': The three quantum numbers labeling an atomic orbital can be used equally well to define its energy, shape and orientation. But all these quantum numbers are not enough to explain the line spectra observed in the case of multi-electron atoms, that is, some of the lines actually occur in doublets (two lines closely), triplets (three lines, closely spaced) etc. This suggests the presence of a few more energy levels than predicted by the three quantum numbers.

In 1925, George Uhlenbeck and Samuel Goudsmit proposed the presence of the fourth quantum number known as the **electron spin quantum number (m_s).** An electron spins around its own axis, much in a similar way as earth spins around its own axis while revolving around the sun. In other words, an electron has, besides charge and mass, intrinsic spin angular quantum number. Spin angular momentum of the electron – a vector quantity, can have two orientations relative to the chosen axis. These two orientations are distinguished by the spin quantum numbers m_s which can take the values of +1/2 or -1/2. These are called the **tow spin states of the electron** and are normally represented by two arrows, ↑(spin up) and ↓ (spin down). Two electrons that have different m_s values (one +1/2 and the other -1/2) are said to have opposite spins. An orbital cannot hold more than two electrons and these two electrons should have opposite spins.

To sum up, the four quantum numbers provide the following information:

(i) n defines the shell, determines the size of the orbital and also to a large extent the energy of the orbital.
(ii) There are n sub-shell in the n^{th} shell. l identifies the sub-shell and determines the shape of the orbital. There are (2l+1) orbitals of each type in a sub-shell, that is, one s orbital (l=0), three p orbitals (l=1) and five d orbitals (l=2) per sub-shell. To some extent l also determines the energy of the orbital in a multi-electron atom.
(iii) m, designates the orientation of the orbital. For a given value of l, m_1 has (2l+1) values, the same as the number of orbitals per sub-shell. it means that the number of orbitals is equal to the number of ways in which they are oriented.
(iv) M_s refers to orientation of the spin of the electron.

Filling of Orbitals in Atom

The filling of electrons into the orbitals of different atoms takes place according to the aufbau principle.

Aufbau Principle

In the ground state of the atoms, the orbitals are filled in order of their increasing energies.

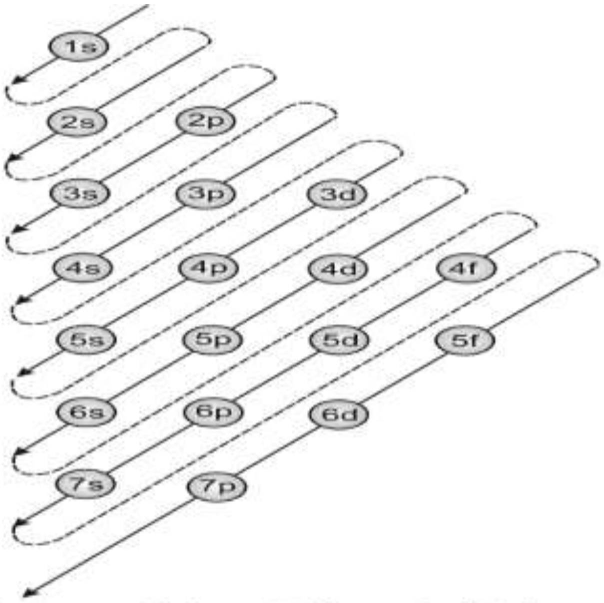


Fig.: *Order of filling of orbitals*

Pauli Exclusion Principle

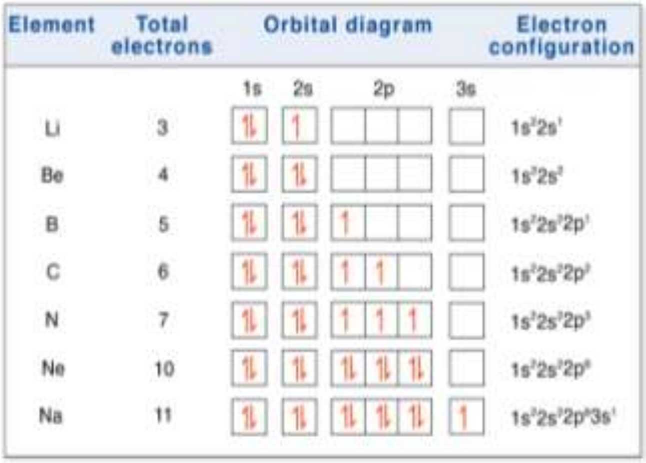
No two electrons in an atom can have the same set of four quantum numbers. “only two electrons may exist in the same orbital and these electrons must have opposite spin”. The maximum number of electrons in the shell with principal quantum number n is equal to $2n^2$.

Hund’s Rule of Maximum Multiplicity

Pairing of electrons in the orbitals belonging to the same sub-shell (p, d or f) does not take place until each orbital belonging to that sub-shell has got one electron each i.e., it is singly occupied.

Electronic Configuration of Atoms

The distribution of electrons into orbitals of an atom is called its **electronic configuration.**



Element	Total electrons	Orbital diagram						Electron configuration
		1s	2s	2p			3s	
Li	3	⇅	↑					$1s^2 2s^1$
Be	4	⇅	⇅					$1s^2 2s^2$
B	5	⇅	⇅	↑				$1s^2 2s^2 2p^1$
C	6	⇅	⇅	↑	↑			$1s^2 2s^2 2p^2$
N	7	⇅	⇅	↑	↑	↑		$1s^2 2s^2 2p^3$
Ne	10	⇅	⇅	⇅	⇅	⇅		$1s^2 2s^2 2p^6$
Na	11	⇅	⇅	⇅	⇅	⇅	↑	$1s^2 2s^2 2p^6 3s^1$

The electrons in the completely filled shells are known as core electrons and the electrons that are added to the electronic shell with the highest principal quantum number are called **valence electrons.**