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ATOMIC STRUCTURE

1.1 FUNDAMENTAL PARTICLES OF ATOM

The *Atomic Theory of Matter* states that all matter consist of extremely small particles called atoms. The atom is the fundamental building block of all 'matter'. An individual atom is very small. In fact, the smallest atom, hydrogen, has a diameter of 10^{-8} cm. Atoms of all elements (except hydrogen) contain three fundamental particles, namely protons, neutrons and electrons. In the hydrogen atom, there is only one proton and an electron. Protons and neutrons are present in the central core of the atom, called the *nucleus*, while electrons revolve around the nucleus in fixed paths known as *orbits* or *shells* (Fig. 1.1).

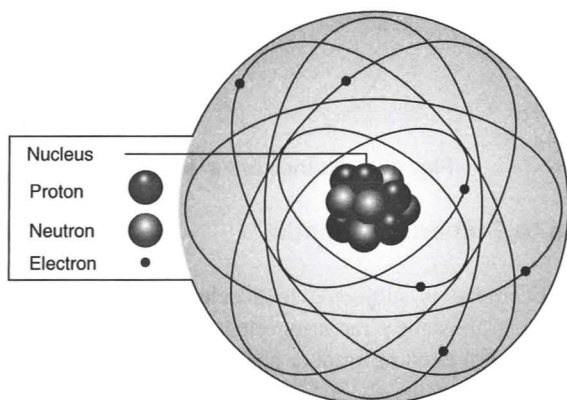


Fig. 1.1 Atomic Structure

- (i) *Proton* It is a positively charged particle having a mass of 1.00728 amu on the C^{12} scale.
- (ii) *Neutron* It is a neutral particle with a mass equal to 1.00866 amu.
- (iii) *Electron* It is a negatively charged particle having negligible mass (1/1836 of the mass of a proton). It has the same magnitude of charge as that of proton but is $-ve$.

Moseley proposed the concept of atomic number. The total number of positive charges present inside the nucleus of an atom is called its *atomic number*.

Atomic number (Z) = Number of protons or Number of electrons

The total number of protons and neutrons present in the nucleus of an atom is called *atomic mass number*.

Atomic mass number (A) = Number of protons + Number of neutrons

1.2 RUTHERFORD'S MODEL OF THE ATOM

Rutherford's model of the atom has the following postulates (Fig. 1.2):

1. Most of the space in the atom is empty.
2. The entire positive charge and mass of the atom is concentrated at its centre known as nucleus. The size of the nucleus is very small when compared to the size of the atom. The size of the atom is of the order 10^{-8} cm and that of nucleus is of the order 10^{-12} to 10^{-13} cm.
3. A sufficient number of electrons are revolving around the nucleus at relatively larger distances from the nucleus.
4. The number of electrons revolving around the nucleus is equal to the number of protons present in the nucleus.
5. Electrons revolve around the nucleus like planets revolve around the sun. Hence, Rutherford's model of an atom is also called as planetary model of an atom and the electrons are called as planetary electrons.
6. The attractive force between electrons and nucleus balances the centrifugal force of the revolving electrons.

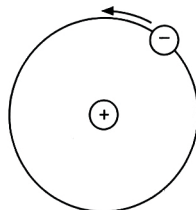


Fig. 1.2 Rutherford's Model

1.2.1 Objections to Rutherford's Model

Whenever an electric charge is subjected to acceleration, it emits radiation and loses energy. In other words, a constantly radiating electron will spiral down into nucleus. As a result of this, the orbit will become smaller and the electrons will drop into the nucleus. This, however, does not happen.

1.3 BOHR'S MODEL OF THE ATOM

In 1913, Niels Bohr proposed a new model of the atom to rectify the defects of Rutherford's model (Fig. 1.3). Bohr's model of atom was based on Planck's quantum theory and was built on the following postulates:

1. The electrons in an atom revolve round the nucleus in definite amount of energy. These orbits are called energy levels. These orbits are numbered as 1, 2, 3 and 4... or named as K, L, M, N... starting from the nucleus.
2. So far as an electron revolves in a certain orbit, its energy remains constant and does not radiate energy. These orbits are called stationary orbits or stationary states.

3. Electrons can revolve only in those stationary states in which their angular momentum is equal to integral multiple of $h/2\pi$, that is

$$mvr = nh/2\pi$$

where m = mass of electron, v = velocity of electron, r = radius of orbit, $n = 1, 2, 3, 4, \dots$, h = Planck's constant.

4. If an electron drops from a higher energy level to a lower energy level, energy is emitted. When an electron jumps from a lower energy level to a higher energy level, energy is absorbed. The absorbed or evolved energy is in the form of quanta, which is equal to the difference in energies of two orbits.

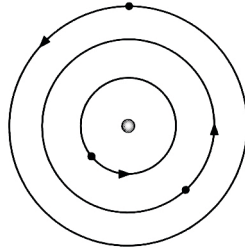


Fig. 1.3 Bohr's Model

$$\Delta E = E_2 - E_1 = h\nu$$

where E_2 = energy of higher orbit, E_1 = energy of lower orbit, h = Planck's constant, ν = frequency.

5. The line spectrum is obtained due to the electronic transition from one stationary orbit to another.

1.3.1 Limitations to Bohr's Theory

Bohr's theory incorporated the concept of quantisation of energy and predicted the existence of discrete atomic energy levels. The theory explained large number of features of spectroscopic data. It, however, had some limitations:

1. It failed to explain the spectra of atoms or ions having more than one electron.
2. Bohr's theory suggested circular, planar orbits (two-dimensional), but actual atomic model has three-dimensional existence.
3. Shapes of molecules arising out of directional bonding could not be explained.
4. Bohr's theory could not explain the fine structure of lines in the spectra (Division of lines observed under a spectroscope of high resolution).
5. Bohr's theory could not explain Zeeman effect and Stark effect.
6. Bohr's theory considered the corpuscular nature for electron but not the wave nature.
7. Bohr's model could not explain the Heisenberg's uncertainty principle.

1.4 SOMMERFELD MODEL

In order to explain the fine structure of the hydrogen spectrum, Sommerfeld proposed elliptical orbits instead of circular orbits (Fig. 1.4).

1. Sommerfeld proposed that the electrons revolve round the nucleus in elliptical orbits. According to the Sommerfeld model, not only do electrons travel in certain orbits but these orbits have different shapes and could tilt in the presence of a magnetic field. Orbits can appear circular or elliptical and can even swing back and forth through the nucleus in a straight line.

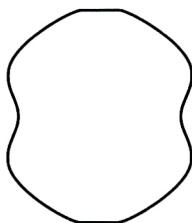


Fig. 1.4 An Elliptical Orbit

2. The electron travelling in an elliptical orbit possesses angular momentum. This angular momentum is quantified.

1.5 WAVE NATURE OF THE ELECTRON

The planetary theory of atomic structure forwarded by Rutherford and Bohr considers the electrons as particles moving in orbits around the nucleus. In the 1920s, it was shown that moving particles such as electrons behaved in some ways as waves. Following observations further substantiated this dual nature of electrons:

1. Light also has a dual nature. Some metals such as potassium emit electrons when irradiated with light of particular wavelength. This phenomenon is called photoelectric effect. It is explained by light travelling as particles called photons. When a photon collides with an electron, it can transfer its energy to the electron. If the energy of the photon is sufficiently large, it can remove the electron from the surface of the metal.
2. However, the phenomena of diffraction and interference of light can only be explained by assuming that light behaves as waves.
3. In 1924, de Broglie postulated that this dual character is applicable to electrons. The photoelectric effect indicates the particle nature of electrons while electron diffraction gives evidence for their wave nature. Diffraction rings were observed photographically when a stream of electrons was passed through a thin metal foil. Considering wave nature of electrons, the concept of wave mechanics has been developed which explains the electronic structure of atoms.

1.6 HEISENBERG UNCERTAINTY PRINCIPLE

According to classical mechanics, the position and momentum of a moving electron can be determined with great accuracy. In 1927, Werner Heisenberg developed a completely different approach to atomic theory; formulated an important feature of wave mechanics and gave the relationship between the position and momentum of a particle. If position

is determined accurately, the momentum becomes less accurately known. Hence certainty of determination of one property introduces uncertainty of determination of the other.

If Δx and Δp are uncertainties in position and momentum of an electron respectively, Heisenberg showed that their product, i.e. product of uncertainty in position and uncertainty in momentum could never be smaller than $h/2\pi$, that is

$$\Delta x \times \Delta p \geq h/2\pi$$

It is impossible to determine accurately both the position and momentum (or velocity) of particle (e.g. electron) simultaneously. It is expressed as

$$\Delta x \cdot p \geq h/2\pi$$

$$\Delta x \cdot m\Delta v \geq h/2\pi$$

where Δx = uncertainty in position, Δp = uncertainty in momentum, Δv = uncertainty in velocity, m = mass of the particle, h = Planck's constant.

1.7 ELECTRONIC CONFIGURATION

The distribution of electrons among the orbitals of an atom is called the electronic configuration. It is obtained by the application of Pauli's exclusion principle, the order of filling the orbitals or relative energies of orbitals. The electronic configuration of atoms of various elements, in their ground state, is governed by the following principles/rules:

1. *The Pauli's exclusion principle* The Pauli's exclusion principle was postulated in an attempt to explain some of the properties of electrons in an atom. This principle states that in an atom no two electrons can have identical four quantum numbers. This is an example of a general principle, which applies, not only to electrons but also to other particles (actually, protons and neutrons obey the same principle, while photons do not). By 'state' here we mean a set of properties, such as energy that characterises an electron.

This principle applies to more complex atoms containing more than one electron. However, in these atoms a complication arises, in that a more rigorous treatment of the problem of an electron orbiting about a proton reveals that, for *each* value of the integer n of the Bohr model, there can be $2n^2$ distinct states that a given electron can occupy.

2. *Aufbau's principle* Aufbau's principle states that in the building up of atom, the added electron will occupy an available orbital of lowest energy. According to this principle, the atoms are constructed by adding a proton to the nucleus and an electron to the sub-shell that has the least energy. The sub-shells are filled in the increasing order of energy. The ascending order is

$$1s; 2s, 2p; 3s, 3p; 4s, 3d, 4p; 5s, 4d, 5p; 6s, 4f, 5d, 6p; 7s, 5f, 6d, 7p$$

3. *Hund's rule* Electron pairing in any s , p , d or f orbital is not possible until all the available orbitals of the same sub-shell contain one electron each. An electron occupies a vacant orbitals in the same sub-shell and pairing can start when all orbitals are filled up. In other words, electrons fill each and all orbitals in the sub-shell before they pair up with opposite spins.

1.8 QUANTUM NUMBERS

To explain an electron completely in an atom, four numbers known as quantum numbers are required. In other words, quantum numbers give the complete identity of an electron in an atom. They are:

1. Principal quantum number
2. Azimuthal quantum number
3. Magnetic quantum number
4. Spin quantum number

1. **Principal Quantum Number** The principal quantum number was introduced by Niels Bohr and designated by n . It represents the main electronic energy shells from nucleus. It can take only integral values like 1, 2, 3, 4, . . . , etc. The corresponding shells are also designated by the English alphabets K, L, M, N, etc.

The principal quantum number gives the size of the orbit. As the value of n increases the size of the electron orbit and its energy increases. The maximum number of electrons that can accommodate in a given orbit is known by $2n^2$, where n is the number of the orbit. Thus, the first shell can accommodate $2 \times 1^2 = 2$ electrons, the second shell, $2 \times 2^2 = 8$, the third shell, $2 \times 3^2 = 18$ and so on.

2. **Azimuthal Quantum Number** Azimuthal quantum number is also called subsidiary or orbital or secondary or angular momentum quantum number which is represented by l . Sommerfeld introduced this quantum number to represent the number of sub-shells in a shell. These sub-levels or orbitals are symbolised by letters s , p , d and f , respectively. The number of sub-shells in any shell can have the values 0 to $(n - 1)$. For example, for principal quantum number $n = 1$, the only possible value for $l = 0$, i.e. there is only one possible orbital (s orbital). For $n = 2$, there are two possible values of l ($l = 0$; $l = 2 - 1 = 1$). Again, $l = 0$ represents s orbital and $l = 1$ indicates a p orbital.

Sub-shell	Number of Orbitals
s	1
p	3
d	5
f	7

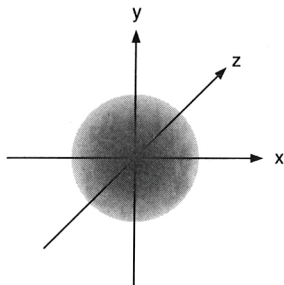
3. **Magnetic Quantum Number** Magnetic quantum number was introduced to explain the number of orbitals in a sub-shell. Magnetic quantum number is denoted by the letter m . It can have all the integral values from -1 to $+1$ through zero. For each value of l , there will be $(2l + 1)$ values of m .

Sub-shell	Azimuthal Quantum Number (l)	Magnetic Quantum Number (m)	Number of Orbitals ($2l + 1$) Values
s	0	0	1
p	1	$-1, 0, +1$	3
d	2	$-2, -1, 0, +1, +2$	5
f	3	$-3, -2, -1, 0, +1, +2, +3$	7

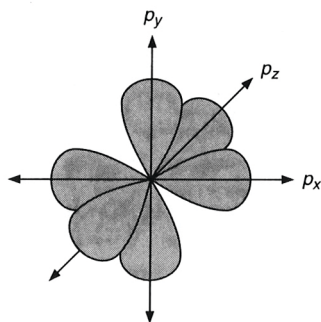
4. **Spin Quantum Number(s)** In 1925, Uhlenbeck and Goudsmit proposed that when an electron rotates around the nucleus, it also spins about its own axis. An electron can spin either clockwise or anticlockwise. Hence s can have two values $+\frac{1}{2}$ and $-\frac{1}{2}$ depending upon the direction of spin. Arrows also represent the direction $\uparrow\downarrow$. The two electrons with the same sign of the spin quantum numbers are said to have parallel spins and that have opposite sign of spin quantum numbers are said to be anti-parallel spin or paired-up spin.

1.9 ATOMIC ORBITALS

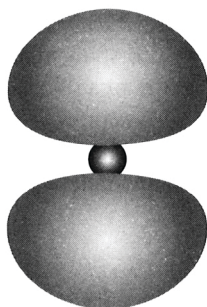
The shape and size of the region in space around the nucleus, where the probability of finding an electron with certain energy is maximum is called an orbital. There are four types of orbitals that is s , p , d and f . All these four types of orbitals must possess a characteristic shape of their own. According to Schrödinger's wave equation an s orbital has a spherical shape with the nucleus lying at its centre. s orbitals in the quantum levels are spherically symmetrical. The size of s orbital increases with n (principal quantum number) value.



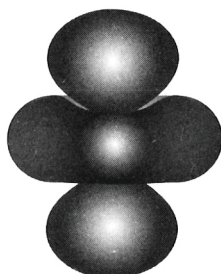
There are three p orbitals in each principal quantum level corresponding to $m = -1, 0, +1$. In p_x orbital, the two lobes are symmetrically oriented along the x -axis. In p_y and p_z , the orientation along y -axis and z -axis, respectively. These three p orbitals are of same energy and are called *degenerate orbitals*.



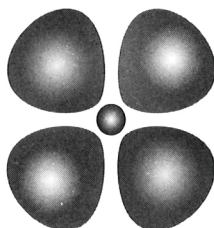
A p orbital has a dumb-bell shape with two lobes disposed symmetrically about the nucleus along a line. This line is referred to as the orbital axis. The two lobes of the orbital have a position concentric with the atomic nucleus where the probability of finding an electron is zero. This point is termed as a *node* and the plane passing through it is called a nodal plane.



In addition to s and p orbitals, there are two other sets of orbitals (d and f) which become available for electrons to inhabit at higher energy levels. At the third level, there is a set of five d orbitals (with complicated shapes and names) as well as the $3s$ and $3p$ orbitals ($3p_x$, $3p_y$, $3p_z$). These five orbitals in each level corresponding to $m = -2, -1, 0, +1, +2$. At the third level there are a total of nine orbitals altogether. These are orbitals corresponding to $l = 2$ and are designated as d_{xy} , d_{yz} , d_{zx} , d_{x^2} , d_{y^2} , d_{z^2} .

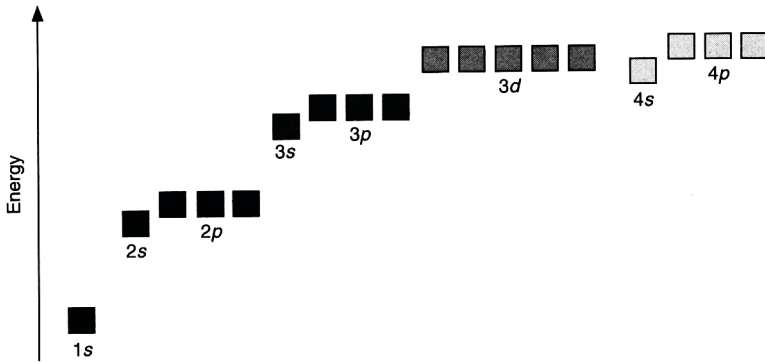


At the fourth level as well the $4s$ and $4p$ and $4d$ orbitals there are an additional seven f orbitals, i.e. 16 orbitals in all. s , p , d and f orbitals are then available at all higher energy levels as well. The f orbitals start from the fourth quantum level, i.e. $n = 4$. The Azimuthal quantum number is $l = 3$. The magnetic quantum numbers are $m = -3, -2, -1, 0, +1, +2, +3$. These orbitals have complicated shapes.



1.9.1 The Order of Filling Orbitals

Electrons fill low energy orbitals (closer to the nucleus) before they fill higher energy ones. Where there is a choice between orbitals of equal energy, they fill the orbitals singly as far as possible. The diagram summarises the energies of the orbitals up to the $4p$ level.



The s orbital always has a slightly lower energy than the p orbitals at the same energy level, so the s orbital always fills with electrons before the corresponding p orbitals. The real oddity is the position of the $3d$ orbitals. These are at a slightly higher level than the $4s$ and so it is the $4s$ orbital, which will fill first, followed by all the $3d$ orbitals and then the $4p$ orbitals.

PRACTICE QUESTIONS

1. Explain the fundamental conflict between Bohr's model of hydrogen atom and Heisenberg's uncertainty principle.
2. State and explain Heisenberg's uncertainty principle. Explain why wave nature is observed in small particles only.
3. Describe the wave nature of an electron.
4. What is de Broglie concept.
5. Write notes on:
 - (a) s orbital
 - (b) p orbital
 - (c) d orbital
6. What are the limitations of Bohr's theory?
7. Explain Pauli's exclusion principle and Hund's rule taking oxygen as an example.
8. What is the maximum number of electrons with the principal quantum number 3? How are these distributed in an atom?
9. Explain quantum numbers and wave nature of electrons.
10. Write the importance of quantum numbers.