Unit 2

STRUCTURE OF ATOM

2.1 Introduction

Different scientists have thought logically about the structure of atom and have given an accepted nuclear model which is known as 'Nuclear model'. This model is derived from the characteristics based on experimental results.

The existence of atom has been proposed since the time of early Indian and Greek philosophers who were of the view that atoms are the fundamental building blocks of matter. According to them atoms are formed due to continuous subdivision of matter into subconstituents which are indivisible. The word 'atom' has been derived from the Greek word 'a-tomio' which means 'uncuttable' or indivisible. This ideology could not last long and was revived by scientists in the nineteenth century.

The atomic theory of atom was first proposed in 1808 by a British scientist John Dalton, which is known as Dalton's atomic theory. According to him atom is the ultimate particle of matter.

2.2 Fundamental Particles : Proton, Electron and Neutron

Dalton's atomic theory was able to explain the law of conservation of mass, law of constant proportion and law of multiple proportion successfully; but failed to explain some experimental results e.g. when glass is rubbed with silk or ebonite with fur it generates electricity. Thus Dalton's theory was only based on assumptions but it did not have any support of experimental results.

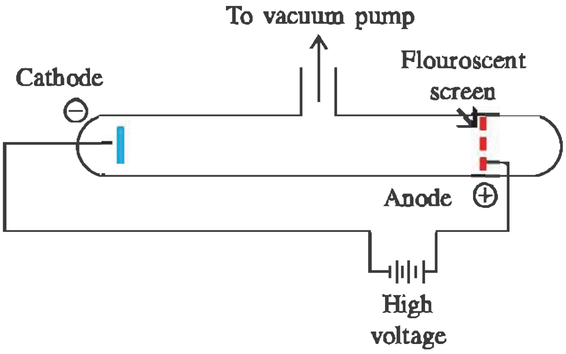
It is proved from modern research that atom is divisible and can be divided into two parts :

(1) Central part of an atom

(2) Region other than central part of an atom

2.2.1 Discovery of Electron : In 1830, Michael Faraday showed that when electric current is passed through a solution of an electrolyte, chemical reactions occur at the electrodes which result in the liberation and deposition of matter at electrodes.

An insight into the structure of atom was obtained from the experiments on electrical discharge through gases. Michael Faraday studied electrical discharge in an evacuated tube



A cathode ray discharge tube with perforated anode.

Figure 2.1

as shown in figure 2.1. A cathode ray tube is made of glass containing two thin pieces of metal called electrodes, sealed in it. When sufficient electricity at high voltage is passed through sealed electrodes, current starts to flow through a stream of particles moving in the evacuated tube from the negative electrode (cathode) to the positive electrode (anode). They are known as cathode rays or cathode particles. These cathode rays can be examined by allowing them to strike on phosphorescent screen. The characteristic cathode rays (which were later on known as electrons) do not depend upon the material of electrodes or nature of gas in the cathode ray tube. Thus, electrons are fundamental constituents of structure of all atoms.

2.2.2 Proton and Neutron : The study of cosmic rays and nuclear reactions of atom proved that atom can be divided into subatomic particles like proton, electron and neutron. These three particles are known as fundamental particles of atom. In addition to these three main subatomic particles, some other subatomic pacticles like positron, photon, graviton, meson etc. are also present.

It was proved by Faraday's electrolysis experiment and cathode ray discharge tube that proton (p^+) remains within the nucleus of an atom while electron (e^-) in the outer region of atomic nucleus. The fundamental particles were discovered by different scientists. Proton (p^+) was discovered in 1886 by Goldstein while electron (e^-) was discovered by J.J Thomson in 1897. Neutron (n) was discovered by Chadwick in 1932. Properties of these fundamental particles are given in table 2.1.

Name	Electron	Proton	Neutron
Symbol	e	p	n
Absolute charge	-1.6022×10^{-19}C	$+1.6022\times10^{-19}$C	0
Relative Electric charge	–1	+1	0
Mass (kg)	9.10939×10^{-31}	1.67262×10^{-27}	1.67493×10^{-27}
Mass (u)	0.00054	1.00727	1.00867
Approxi-mate mass (u)	0	1	1

C = coulomb; u = a.m.u.

2.3 Atomic Number, Atomic Mass, Isotope, Isobar and Isotone

Atoms (except hydrogen) contain mainly three fundamental particles proton, electron and neutron. Since all elements and compounds have mass; atom also has mass. The total mass of an atom is concentrated in a nucleus which has very small volume (compared to the total volume of the atom). Electrons are arranged in the outer part of nucleus.

The positive charge of nucleus is due to protons (which are positively charged) because neutrons are electrically neutral. The charge on the proton is equal but opposite to that of electron. The number of protons present in the nucleus of an atom is called atomic number (Z) e.g. Number of protons in the nucleus of the very first element of periodic table hydrogen atom is one, and therefore, atomic number of hydrogen element is one.

As atom is electrically neutral, number of protons and number of electrons in an atom are always equal.

Atomic number (Z) = number of protons in the nucleus of atom
OR
number of electrons in a neutral atom.

Mass of nucleus is due to proton and neutron (as mass of the electron is negligible). Protons and neutrons which are present in the nucleus are collectively known as 'nucleons.' Thus mass number or atomic mass number (A) of an element is equal to the number of nucleons.)

Mass number **or** Atomic mass = Number of protons(Z) + Number of neutrons (n)

e.g. Atomic mass of sodium is 23. Its atomic number is 11, therefore number of neutrons

= 23 – 11 = 12

Atomic mass and atomic number of any element (X) are indicated by accepted symbols. Accordingly, element is represented by X with superscript on left hand side as the atomic mass number (A) and subscript (Z) on left hand side as the atomic number.

$^{A}_{Z}X$ A = Atomic mass number

Z = Atomic number

X = Symbol for element.

Isotopes : Isotopes are species with identical atomic number but different atomic masses. In other words, the difference in atomic mass or mass number in isotopes is due to different number of neutrons present in the nucleus. 99.985% hydrogen contains one proton. This isotope is known as protium $^{1}_{1}H$. Rest of the percentage of hydrogen atom contains two other isotopes. the one containing 1 proton and 1 neutron which is deuterium $^{2}_{1}H$ or $^{2}_{1}D$ (0.0156%) and the third containing 1 proton and 2 neutrons which is known as tritium $^{3}_{1}H$ or $^{3}_{1}T$ (10^{-15}%). Earth's crust contains very small amount of tritium. These three isotopes of hydrogen can be symbolically represented as

$$^{1}_{1}H;\ ^{2}_{1}D;\ ^{3}_{1}T$$

One of the important fact regarding the isotope is that the chemical properties of an atom depends on number of electrons and which are determined by number of protons in the nucleus. Hence, chemical properties of isotopes of a given element are identical.

Isobars : Isobars are the species having same mass number (atomic mass) but different atomic number e.g. $^{14}_{6}C;\ ^{14}_{7}N$

Isotones : Isotones are species having same number of neutrons but different numbers of atomic mass and atomic number

e.g. $^{30}_{14}Si;\ ^{31}_{15}P;\ ^{32}_{16}S$

Example 2.1 : Calculate number of protons, electrons and neutrons in $^{31}_{15}P$

Solution :

Atomic number Z = 15 in $^{31}_{15}P$ and atomic mass A = 31. Number of protons = number of electrons in atom Z = 15

∴ Number of neutrons = Atomic mass – number of protons

= 31 – 15

∴ Number of neutrons = 16

Example 2.2 : The number of electrons, protons and neutrons in a given species are equal to 15, 10, and 8 respectively. Assign proper symbol to the species.

Solution :

Number of proton = 8 = Atomic number

Therefore the given species is oxygen element

Atomic mass = Number of proton + Number of neutrons

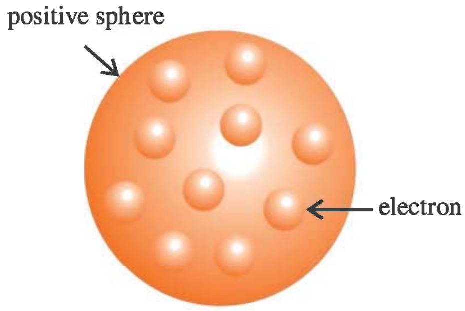
(mass number) = 8 + 8 = 16

Atomic mass = 16

The given species is not neutral because number of protons (8) and number of electrons (10) are not equal. Hence it becomes negative ion with two units of negative charge. As a result symbol of this species will be $^{16}_{8}O^{2-}$.

2.3.1 Thomson's Model of Atom and its limitations :

J.J. Thomson, in 1898, first proposed about the spherical shape (radius approximately 10^{-10}m) of an atom, in which the positive charge is uniformly distributed. Electrons are embedded in such a way that they give most stable electrostatic arrangement. Many different names are given to this model, for example, plum pudding, raisin pudding or watermellon.



Thomson's model of an atom

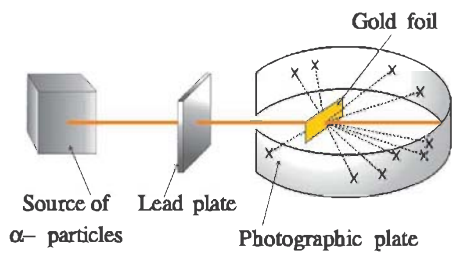
Figure 2.2

According to this model, positively charged proton and negatively charged electrons are symmetrically distributed over atom. In this model number of protons and electrons arranged symmetrically are equal. One of the important features of this model is that the total mass of an atom is distributed equally. This model explains overall electrical neutrality of an atom but is not consistent with the experimental results. Thomson was awarded Nobel Prize in physics, in 1906, for theoretical and experimental research on electrical conduction of gases.

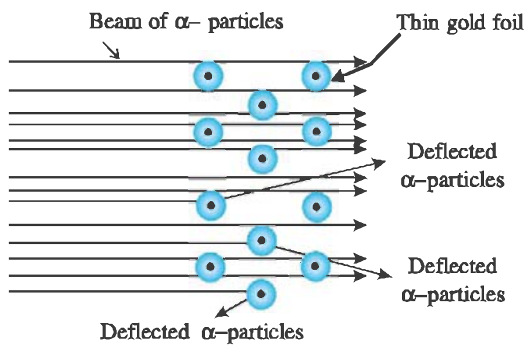
Limitations of Thomson's model of an atom :

According to Thomson's model of an atom, we have seen that protons, electrons and neutrons are equally arranged. But from the Rutherford's α- particle scattering experiment it was noted that most of the space in an atom is empty because most of the α- particles passed through metal foil without reflection. Thus, Thomson's model of an atom could not explain α- particle scattering phenomenon.

2.3.2 α- Particle scattering experiment and Rutherford's model of an atom and its limitations : Rutherford's model of an atom is also known as nuclear model of an atom. Rutherford and his students Hans Geiger and Ernest Marsden bombarded α- particle on thin gold foil. This well known α- particle scattering experiment is shown below :



a. Rutherford's α- particle scattering expriment



b. Schematic view of Rutherford's α- particle scattering expriment

Figure 2.3

High energy α- particles from radioactive source were directed upon a thin foil (thickness 100 nm) of gold metal. A fluorescent zinc sulphide screen was kept around the thin gold foil. When α- particles struck this screen they produced fluorescence effect. The result of this experiment was quite unexpected because according to Thomson's model of atom the mass of each gold atom in the foil should have been spread evenly over the entire atom and α-particles should have sufficient energy to pass directly through such a uniform distribution of mass. According to Thomson, when α- particles pass through a foil, they would slow down and change directions angularly. It was noted from Rutherford's experiment that.

(i) Most of the α- particles passed through the gold foil were undeflected.

(ii) Very less α- particles were deflected with angle.

(iii) A few α- particles (1 in 20,000) bounced back.

On the basis of the experimental observations, Rutherford drew the following conclusions for atomic model.

(i) As majority of the α-particles pass through the foil, most of the space in atom remains empty.

(ii) A few positively charged α-particles are deflected which is due to repulsion. The positive charge of atom is concentrated in a very small volume which is responsible for the deflection of positively charged α-particles. It is known as nucleus of atom.

(iii) The size of an atomic nucleus is negligible compared to the size of an atom. Atomic radius is about 10^{-10}m while that of nucleus is 10^{-15}m.

On the basis of above observations and conclusions, Rutherford proposed the nuclear model of atom. According to this model :

(i) The positive charge and most of the mass of the atom is concentrated in the center in an extremely small region. This small region was called nucleus by Rutherford.

(ii) Electrons move around the nucleus with a high speed in a circular path called an orbit.

(iii) Electrons and nucleus are held together by electrostatic forces of attraction.

Drawbacks of Rutherford's atomic model :

The Coulombic force $k\frac{q_1q_2}{r^2}$ where q_1 and q_2 are the charges, r is the distance of separation of the charges and k is the proportionality constant between electron and the nucleus is mathematicaly similar to the gravitational force $G\frac{m_1m_2}{r^2}$ where m_1 and m_2 are the masses, r is the distance between masses and G is the gravitational constant .The similarity between solar system and nuclear model suggests that electrons should move around the nucleus in some definite orbits. Now, when anything moves in orbit, it accelerates (substance gets accelerated even though moving with a constant speed due to change in the direction). Thus electron in a nuclear model describing planet like orbits also accelerates.

There is no phenomenon of attraction or repulsion in planet (since they are uncharged). But attractive and repulsive forces between positively charged nucleus and negatively charged electrons should be considered.

According to the electromagnetic theory of Maxwell, charged particles when accelerated should emit electromagnetic radiation (this feature does not exist for planet since they are uncharged). Therefore, when an electron in orbit emits radiation, the energy of radiation comes from electronic motion. Thus orbit shrinks. Calculation shows that electron takes only 10^{-8} s to get attracted into the nucleus. But this does not happen. Thus Rutherford's model can not explain stability of an atom. Another major drawback of the Rutherford's model is that no information about the electronic structure of atom can be obtained i.e. how electrons are distributed in an atom. The nucleus and energy possessed by them remain unknown.

2.4 Nature of Electromagnetic Radiation

Light is known as electromagnetic radiation. To explain the observations of the experiments in this field scientist Max Planck suggested, in 1900, that light has particle nature. Afterwards scientist Huygens proposed the wave nature theory of light on the basis of phenomena like interference and diffraction. Scientist Albert Einestein in 1902 studied the emission of electrons from the surface of the metal by light. This effect of light is known as photoelectric effect. Albert Einstein suggested that quantum properties, absorption and emission can be applied to radiation also. This means that electromagnetic radiation should be made up of particles which are known as photon. The relation between energy (E) of photon and the frequency (ν) of light is as follows:

$$E=h\nu$$

The relation between frequency (ν) and wavelength (λ) of light is as follows:

$$\nu = \frac{c}{\lambda}$$

Hence, the energy of photon $E = \frac{hc}{\lambda}$

where, E = energy of photon
c = velocity of light
h = Planck's constant
λ = wavelength

The energy possessed by 1 mole of photon is known as one Einstein.

$\therefore NE = \frac{Nhc}{\lambda}$ (where N = Avogadro number)

2.5 Emission Spectra of Hydrogen Atom

Light is emitted when high voltage of electricity is applied to hydrogen gas kept in electric discharge tube under controlled conditions and low pressure. This emitted light appears to be of light purple colour. If it is analysed by an instrument called spectrograph, different series of lines at different distances are obtained in the spectrum. These lines obtained in the spectrum are called line spectra. The characteristic line spectra obtained by emission of light from any other element in geseous state like that in hydrogen is known as atomic spectra.

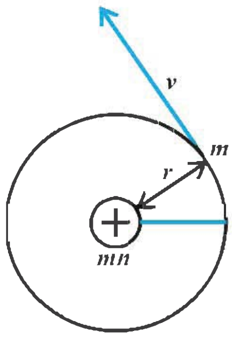
At the first sight hydrogen spectrum appears to be complicated. The regularity in the positions of the lines in the series is proved. These series are known as Lyman, Balmer, Paschen, Brackett and Pfund series from the names of scientists who have discoverd them.

2.6 Bohr's Atomic Model and Its Limitations

Niels Bohr (1885-1962) : Niels Bohr, the Danish physicist, received Ph.D. from the University of Copenhagen in 1911. He then spent a year with J.J. Thomson and Ernest Rutherford in England in 1913, He returned to Copenhegan where he remained for the rest of his life. In 1920 he became the Director of the Institute of Theoretical Physics. After World War-I Bohr worked enthusiastically for peaceful uses of atomic energy. He received peace award in 1957. Bohr was awarded Nobel Prize in physics in 1922.

From the study of matter, radation, more information about the structure of atom and models can be obtained. Niels Bohr applied these results to modify Rutherford's model.

Bohr was the first one to propose atomic model for hydrogen atom and it was the first attempt to describe arrangement of electrons in an atom. According to Bohr, hydrogen contains one proton in its nucleus and its one electron continuously revolves around the nucleus in definite path called orbit. Nucleus of the atom gets positively charged due to presence of proton and electron gets negative charge; so a force of attraction is produced between them. As a result possibility of electron to enter in to nucleus arises. If the distance between nucleus and electron (which is also known as radius of orbit) is increased, attraction between them decreases. As a result energy of electron also decreases.



Bohar's model of an atom
Figure 2.4

To explain hydrogen spectrum Bohr gave following postulates :

(i) Electron revolves around the nucleus in certain accepted (permissible) energy states (orbits). Eventhough electron continuously revolves around the nucleus in some definite orbit, its energy remains constant. The path of electron revolution where its energy remains constant is known as stationary state or stationary orbit. Thus, energy is neither absorbed nor emitted when electron revolves in stationary orbit.

(ii) Electron can move from one stationary orbit to another either by absorbing or emitting energy. The amount of energy absorbed or emitted by electron remains constant

$E_1 + h\nu \rightarrow E_2$ Absorption of energy

$E_2 \rightarrow E_1 + h\nu$ Emission of energy.

where, E_1 = lower energy stationary orbit

E_2 = higher energy stationary orbit

h = Planck's constant

ν = frequency of radiation

$E_1 \uparrow E_2$ Energy absorption

$E_2 \downarrow E_1$ Energy emission

(iii) Electron can revolve only in such orbit in which its angular moment $h/2\pi$ is an integral multiple of n where n is any positive integral number n = 1, 2, 3, ...n. This type of orbit is called accepted or permissible orbit.

$$\text{Angular momentum} = mvr = \frac{nh}{2\pi} \qquad 2.1$$

where, m = mass of electron

v = velocity

r = radius of orbit (distance between electron and nucleus)

n = positive integer number

h = Planck's constant

(iv) Energy of electron revolving in accepted or permissible orbit, E, can be given by Bohr's equation

$$E = \frac{-\,2e^4\pi^2Z^4m}{n^2h^2} \qquad 2.2$$

where, E = energy of electron

h = Planck's constant

e = charge of electron

Z = atomic number

m = mass of electron

n = any positive integer number

The negative sign in the above equation indicates that energy of electron in an atom is less than energy of free electron. Free electron remains at far distance from the nucleus and its energy is considered to be zero. For hydrogen atom, energy states n>1 are considered as excited states of electron.

(v) The most important property associated with the electron is the energy of its stationary state which is given by following equation :

$$E_n = -R_H\left(\frac{1}{n^2}\right) \quad n = 1,2,3 \qquad 2.3$$

where R_H = Rydberg's constant = 2.18×10^{-18}J

n = 1, 2, 3,. . . . n

The energy of the lowest state also called the ground state is,

$$E_1 = -2.18 \times 10^{-18}\left(\frac{1}{1^2}\right) J$$

$$E_1 = -\,2.18 \times 10^{-18} J$$

The energy of the stationary state for n = 2, will be

$$E_2 = -2.18 \times 10^{-18}\left(\frac{1}{2^2}\right)\ J$$

$$E_2 = -\,0.545 \times 10^{-18} J$$

(vi) Electron can move from one energy state to another either by absorption of energy or emission of energy. The energy difference is ΔE which can be given as

$$\Delta E = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$\Delta E = 2.18 \times 10^{-18} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

where, R_H = Rydberg's constant

n_i = initial energy state

n_f = final energy state.

Frequency associated with energy absorption or emission can be given as

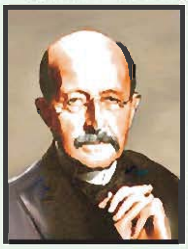
$$\Delta E = h\nu = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad 2.4$$

$$\therefore \nu = \frac{\Delta E}{h} = \frac{R_H}{h} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$\therefore \nu = \frac{2.18 \times 10^{-18}}{6.626 \times 10^{-34}} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$\therefore \nu = 3.29 \times 10^{15} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \text{Hz} \quad 2.5$$

Max Planck (1858-1947) :



Max Planck, the German physicist, received degree of Ph.D. in theoretical physics from the University of Munich in 1879. In 1888, he was appointed as Director of the Institute of Theoretical Physics at the University of Berlin. Planck was awarded the Nobel prize in physics, in 1918, for his quantum theory. Planck also made significant contributions in thermodynamics and other areas of physics.

Example 2.3 : Calculate change in energy of a photon emitted during a transition of electron from n = 4 state to n = 2 state.

Solution :

The initial energy state (n_i = 4) and the final energy state (n_f = 2).

$$\Delta E = 2.18 \times 10^{-18} \times \left(\frac{1}{4^2} - \frac{1}{2^2} \right)$$

$$\therefore \Delta E = -4.076 \times 10^{-19} \text{ J}$$

Explanation of the hydrogen spectrum from Bohr's assumption can be given as follows :

Table 2.2 The spectral lines for atomic hydrogen

Series	n_i	n_f	Range of Spectrum
Lyman	1	2,3....	Ultraviolet
Balmer	2	3,4....	Visible
Paschen	3	4,5....	Infrared
Brackett	4	5,6....	Infrared
Pfund	5	6,7....	Infrared

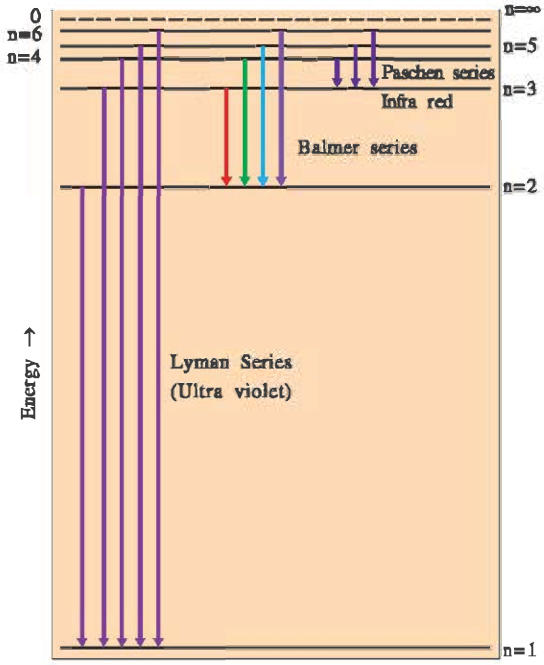


Figure 2.5

Limitations of Bohr's Atomic Model :

Bohr's model of the hydrogen atom is considered as an improvement over Rutherford's nuclear model because it accounts for the stability of atom or ion. Limitations of Bohr's atomic model are as follows :

(i) Bohr's atomic model failed to explain the atomic spectrum of atoms other than hydrogen atom.

(ii) Bohr's model could not give better explanation of hydrogen spectrum because it could not explain the spectrum when two spectral lines are very close to each other (i.e. doublet)

(iii) It failed to explain Zeeman effect i.e. splitting of spectral lines under the influence of magnetic field.

(iv) It could not explain the ability of atoms to form molecule by chemical bonds.

2.7 Dual Nature of Matter and Radiation

James Maxwell (1870) was the first to give comprehensive information about the interaction between the charged substances and the behaviour of electric and magnetic fields on macroscopic level. He suggested that when electrically charged particles move with acceleration, electric and magnetic fields are produced and transmitted. These fields are transmitted in wave forms which are known as electromagnetic waves or electromagnetic radiations.

During time of Newton it was believed that light is made up of particles but in 19th century the wave nature of light was established. Electromagnetic waves are of many types.

Dual Nature of Radiation :

Particle nature of light confused scientists. On one hand it could explain black body radiation and photoelectric effect satisfactorily but on the other hand failed to explain well known phenomena of light like interference and diffraction. To resolve this confusion it was necessary to accept the idea that light possesses both particle and wave like properties, i.e, light has dual behaviour. From the experiment it was decided that light acts as a wave and as a stream of particles.

Example 2.4 : Calculate energy of one mole of photon whose frequency of radiation is 4×10^{14} Hz.

Solution : Energy of one photon can be calculated as follows :

$E = h\nu$

$h = 6.626 \times 10^{-10}\,\text{Js}$

$\nu = 4 \times 10^{14}\ \text{s}^{-1}$

$E = (6.626 \times 10^{-34}\ \text{Js}) \times (4 \times 10^{14}\text{s}^{-1})$

$\therefore\ E = 2.6496 \times 10^{-19}\ \text{J}$

Now, energy of one mole photon

$(E_{mol} = NE)$

$E_{mol} = (2.6496 \times 10^{-19}\ \text{J}) \times (6.022 \times 10^{23}\ \text{mol}^{-1})$

$E_{mol} = 159.0\ \text{kJ mol}^{-1}$.

Example 2.5 : When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium, electrons are emitted with a kinetic energy of 1.68×10^5 J mol^{-1}. What is the minium energy needed to remove an electron from sodium ? What is the maximum wavelength that will cause a photoelectron to be emitted ?

Solution : The energy (E) of a 300 nm photon is given by

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\,\text{Js} \times 3 \times 10^{8}\,ms^{-1}}{300 \times 10^{-9}\,m}$$

$$E = 6.626 \times 10^{-19}\ \text{J}$$

The energy of one mole of photons

$E_{mol} = 6.626 \times 10^{-19}\ \text{J} \times 6.022 \times 10^{23}\ \text{mol}^{-1}$

$E_{mol} = 3.99 \times 10^{5}\ \text{J mol}^{-1}$

The minimum energy to remove one mole of electrons from sodium $= (3.99 - 1.68) \times 10^5\ \text{J mol}^{-1}$

$= 2.31 \times 10^5\ \text{J mol}^{-1}$

The minimum energy for removal of electron

$$E = \frac{2.31 \times 10^5\,\text{J}}{6.022 \times 10^{23}}$$

$\therefore\ E = 3.84 \times 10^{-19}\ \text{J}$

$$\therefore\ \lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34}\,\text{Js} \times 3 \times 10^{8}\,ms^{-1}}{3.84 \times 10^{-19}\,\text{J}}$$

$\therefore\ \lambda = 517\ \text{nm}$

This value of λ =517 nm corresponds to green light.

2.8 De Broglie's Equation

In 1924, French physicist, de Broglie proposed that matter, like radiation also exhibits a dual behaviour. Matter and radiation act both as particle and wave. They possess both particle and wave nature. We know that photon has momentum and wavelength, electrons must also possess momentum and wavelength.

de Broglie gave the following equation relating wavelength and momentum of matter-particle.

$$\lambda = \frac{h}{p} = \frac{h}{m\text{v}} \qquad 2.6$$

where, h = Planck's constant

p = momentum

m = mass of particle

v = velocity of particle

de Broglie's dual character or duality principle was confirmed experimentally. It was found that an electron beam undergoes diffraction which is characteristic of wave. The electron microscope is based on the wave like nature of electron while ordinary microscope utilizes the wave nature of light. Electron microscope achieves a magnification of about 15 million times.

According to this principle, every object in motion has wave character. The wavelengths of ordinary object are so short that their wave properties cannot be detected. The wavelengths associated with electrons and other subatomic particles with very small mass can be detected experimentally.

Example 2.6 : Calculate wavelength of a ball of mass 0.2 kg whose veloicity is 10 ms^{-1}

Solution : According to de Broglie's equation

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\,Js}{(0.2)\,kg \times (10ms^{-1})}$$

$$\lambda = 3.313 \times 10^{-34}\,m = 3.313 \times 10^{-25} nm$$

Example 2.7 : Calculate wavelength of wave associated with electron whose velocity is 10^8 cm sec^{-1}. (Mass of eletron = 9.1×10^{-31}kg)

Solution : $\lambda = \frac{h}{p} = \frac{h}{mv}$

Now, $h = 6.62 \times 10^{-34}\,J$

$m = 9.1 \times 10^{-31} kg$

$v = 10^8\,cm\,sec^{-1} = 10^6 m\,sec^{-1}$

$$\therefore \lambda = \frac{6.62 \times 10^{-34}\,Js}{9.1 \times 10^{-31} kg \times 10^6\,m\,sec^{-1}}$$

$\lambda = 7.27 \times 10^{-10}\,m$

$\lambda = 0.727$ nm

2.9 Heisenberg's Uncertainty Principle

In 1927, German physicist Werner Heisenberg gave uncertainty principle as a consequence of dual behaviour of matter and radiation. It is as follows :

The position and momentum of moving microscopic particle cannot be determined simultaneously and precisely.

When position of electron is measured by electron microscope, the radiation bombarded on electron (radiation possesses energy) is absorbed by the electron and changes its momentum. Similarly, uncertainty in its position is produced when momentum of electron is measured accurately.

A mathematical relationship between uncertainty in position (Δx) and momentum (Δp) was givn by Heisenberg in the form of equation

$$\Delta x \bullet \Delta p \geq \frac{h}{4\pi} \qquad 2.7$$

where,

Δx = uncertainty in position of eletron

Δp = uncertainty in momentum of electron

Now momentum p = m $\times$ v

where, m = mass of electron

v = velocity a electron

Therefore the above equation can also be written as :

$$\Delta x \bullet m\Delta v \geq \frac{h}{4\pi} \qquad 2.8$$

Importance of Heisenberg's uncertainty principle is only for moving microscopic object. This can be explained from the following example :

Suppose Heiserberg's principle is applied to an object having mass of 10^{-8} kg.

$$\Delta v \bullet \Delta x = \frac{h}{4\pi m}$$

$$\Delta v \bullet \Delta x = \frac{6.62 \times 10^{-34}\,Js}{4 \times 3.141 \times 10^{-8}\,kg}$$

$$\Delta v \bullet \Delta x = 0.53 \times 10^{-26}\,m^2s^{-1}$$

Thus the value of $\Delta v \bullet \Delta x$ is extremely small and has no significance. Therefore, one can say that when the mass of any object is of one milligram or more or less, then the uncertainties in momentum or position associated are hardly of any significance.

Particles like electron whose mass is 9.11×10^{-31}kg, the product $\Delta v \bullet \Delta x$ is more and hence for such particles this principle is significant.

$$\Delta v \bullet \Delta x = \frac{h}{4\pi m}$$

$$= \frac{6.0626 \times 10^{-34}\,Js}{4 \times 3.141 \times 9.11 \times 10^{-31}\,kg}$$

$$\Delta v \bullet \Delta x = 10^{-4}\,m^2s^{-1}$$

Therefore, statement of Heisenberg's position and momentum uncertainty is replaced by probability function which is seen in quantum mechanical model of an atom.

Example 2.8 : The position of electron located at $1A^0$ with microscope. Calculate uncertainty in the velocity of electron.

Solution : According to Heisenberg's uncertainty principle,

$$\Delta x \bullet \Delta p = \frac{h}{4\pi}$$

or $\Delta x \bullet m\Delta v = h/4\pi$

$$\therefore \Delta v = \frac{4}{4\pi \Delta x.m}$$

$$\Delta v = \frac{6.626 \times 10^{-34}\,Js}{4 \times 3.14 \times 1 \times 10^{-10} m \times 9.11 \times 10^{-31} kg}$$

$$\Delta v = 5.79 \times 10^5\,ms^{-1}$$

2.10 Explanation of Orbit and Orbital

The circular planar path of rotation of electron around the nucleus is called an orbit. The region around the nucleus of an atom, where probability of finding the eletron is maximum, is called an orbital.

Thus orbital shows probability of finding electron while orbit shows position of electron, its energy and distance of electron from nucleus. Different orbits can be represented by principal quantum number (n).

2.11 Quantum Numbers

In order to describe electron of an atom in detail, quantum numbers are used. The energy levels of electron in atom is mentioned by the use of positive integer number which is known as Principal Quantum Number (n).

Large number of orbitals are possible in an atom. These orbitals can be classified (distinguished) by their size, shape and orientation. Every orbital can be represented mainly by three quantum numbers n, l, and m_l. A new quantum number, i.e. spin quantum number is also introduced based on the rotation of electron around the nucleus as well as spining on its own axis.

Principal quantam number (n) :

Principal quantum number n is positive integer which is represented by n. Its value may be 1, 2, 3.... n. It mainly decides size of orbit and energy up to some extent. Size of orbit and energy of orbit of hydrogen atom and species like hydrogen atom depend only on principal quantum number (n). Number of allowed orbitals increase with increase in n values which are given by n^2. Every orbital for a given value of 'n' constitutes a single shell. They are represented as follows.

n	= 1	2	3	4 .....
Shell	= K	L	M	N .....

Energy of orbit increases with increase in the value of 'n'

Angular Momentum Quantum Number (or Azimuthal Quantum Number) (l) :

Angular momentum or Azimuthal quantum number is represented as 'l'. It is also known as subsidiary quantum number. It decides geometrical shapes of orbitals. For a given value of n, l can have values ranging from 0 to $n-1$ i.e. for a given value of n the possible values of l are $l = 0, 1, 2... (n-1)$.

e.g. $n = 1, \quad l = (n-1) = 1 - 1 = 0$

$n = 2, \quad l = 0, 1$

$n = 3, \quad l = 0, 1, 2,$

Each shell constitutes one or more subshells or sublevels.

The number of subshells in a principal shell is equal to the value of n; e.g. for n = 1 there is only one subshell i.e. l = 0. For n = 2, there are two subshells i.e. l = 0, 1 and so on. Subshells corresponding to n and l are listed in table 2-3, Angular momentum quantum number decides shapes of orbitals,

Value of l	:	0	1	2	3	4	5....
Notation for sub shell	:	s	p	d	f	g	h....

Table 2.3 shows n and l subshell notation.

Table 2.3

n	l	Symbol of sub shell
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 Quantum Number m_l :

Any charged particle (like electron), when is in motion, produces magnetic field which is due to its orbital motion (velocity). The magnetic field value is represented by magnetic quantum number m_l. It indicates orientation of orbitals in space under magnetic field. For a given value of l, m_l values indicate number of specific orbitals i.e. values of m are dependent on l which is given by the following relationship :

e.g. ($m_l = - l$ ..... 0 ..... $+ l$ (i.e. $2l + 1$)

$l = 0, \quad m_l = 0$ (s-orbital)

$l = 1 \quad m_l = -1, 0, + 1,$ (p-orbital)

$l = 2 \quad m_l = -2, -1, 0 + 1, + 2$ (d-orbital)

$l = 3 \quad m_l = -3, -2, -1, 0, +1, +2, +3$ (f-orbital)

Spin Quantum Number 's' :

The above three quantum numbers n, l and m are not enough to explain the line spectra observed in the case of multi-electron atom or ion. e.g. some of the lines occurred in spectrum as doublet or triplet.

In 1925, George Uhlenbeck and Samuel Gouldsmit gave the fourth quantum number known as rotational or spin quantum number 's'.

Electron has two types of motion. Orbital motion in which electron rotates around the nucleus in its own definite orbit. Axial motion is one in which electron spin on its own axis. Velocity of electron around the nucleus is called orbital velocity, but velocity of electron spinning on its axis is known as axial velocity. Electron spin on its own axis either in clockwise or in anticlockwise direction. Hence, value of spin quantum number is taken as +1/2 or –1/2.

Example 2.9 : Find out orbitals associated with principal quantum number n = 3.

Solution :

For n = 3 the possible values of l are 0, 1 and 2 Therefore, there is one 3s-orbital (n = 3, l = 0, m = 0). There are three 3p-orbitals (n = 3, l = 1, m_l = –1, 0, +1). There are five 3d-orbitals (n = 3, l = 2, m_l = + 2, +1, 0, –1, –2). Thus there are total number of orbitals = 1 + 3 + 5 = 9.

(This can also be obtained by using the relation : number of orbitals = n^2 and l = 3^2 = 9)

Example 2.10 : Using s, p d and f orbitals, describe the orbitals with the following quantum numbers :

(a) n = 2, l = 1, (b) n = 4, l = 3, (c) n = 5, l = 0 (d) n = 3, l = 2

Solution :

	n	l	orbital
(a)	2	1	2p
(b)	4	3	4f
(c)	5	0	5s
(d)	3	2	3d

2.12 Shapes of s, p and d-orbitals

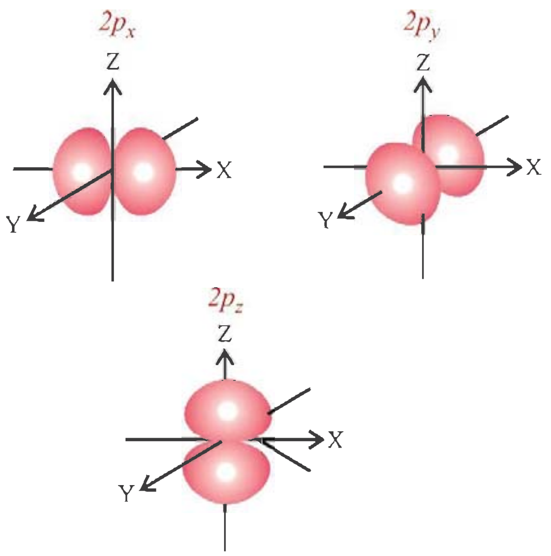
Schrodinger deduced in 1926 the equation for the energy of electron moving around the nucleus which is known as Schrodinger's wave equation : This equation is as follows :

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$$

x, y, and z in the above equation are cartesian co-ordinates showing the position of electron in atom. m = mass of electron, E = total energy of electron-proton system, V = potential energy, h = Planck's constant, Ψ is known as wave function which represents similarity with amplitude of normal wave. There is no physical significance of orbital wave function Ψ of electron. It is only the mathematical function of electron co-ordinate.

As s-orbital is spherically symmetrical, the probability of finding electron in s-orbital is also symmetrical. All the energy levels, having l=0 value, have one spherical orbital which is expressed by symbol ns.

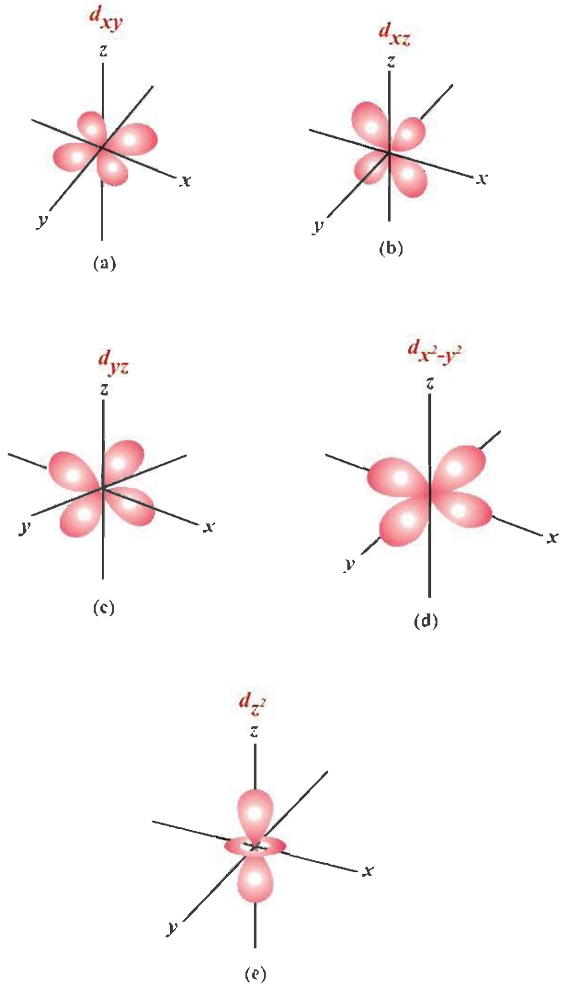
Surface of the orbital where the value of probability function decreases to zero (i.e. probability of finding the electron becomes zero). Such surface is called nodal plane or 'node.' (n–1) indicates number of nodes in ns orbitals. e.g. for n = 1 in 1s orbital there is no node and n = 2 in 2s orbital has 1 node. Boundary surface plot for p orbital (l = 1) is not spherical, but are seen as dumbbell shape. Every p- orbital is divided into two parts which are known as lobes which remain on either side of the plane passing from centre. The probability function is zero at a point where two lobes meet each other. The size, shape and energy of all the three orbitals are equal. They only differ in their orientation. They are named as p_x, p_y and p_z depending upon the lobes lying on x, y or z coordinate. The values of m_l are –1, 0 and +1 respectively.



Boundry surface diagram of the three 2p orbitals

Figure 2.6

Orbitals generated by $l = 2$ values are known as d-orbitals where minimum value of n = 3. It has five equal energy orbitals which are also known as degenerate orbitals. They are named as d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$ and d_{z^2}. The boundry surface diagrams for d-orbital are shown in fig. 2.8.



Boundary surface diagram of the five 3d-orbital

Figure 2.7

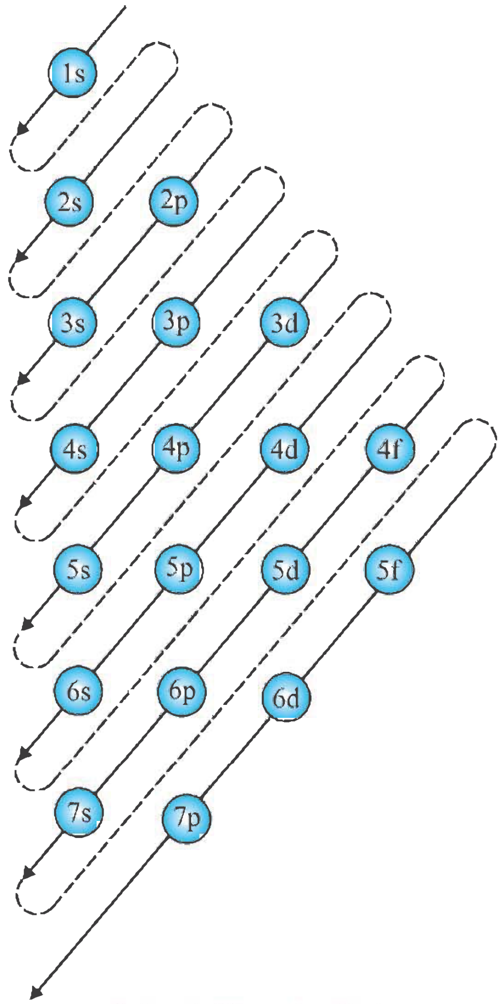
2.13 Rules for the Electron Arrangement in Orbitals

Each atom has definite electron arrangement depending upon the number of electrons present. The distribution of electrons in an atom, in different atomic orbitals is based on some rules, which is known as electron configuration. Electron configuration of atom is mainly followed by three rules :

(i) Aufbau principle (ii) Pauli's exclusion principle (iii) Hund's rule (ie Hund's rule of maximum multiplicity or maximum spin)

(i) Aufbau Principle : The German word Aufbau means 'building up'. We shall use this word in the arrangement of electron in the different orbitals according to their energy.

According to this rule, electron of an atom first enters into the empty orbital of lowest energy. When the lowest energy orbitals are completely filled electron then enters into the orbital of higher energy and this way electrons are arranged in other orbitals based on their energy. Therefore, it is necessary to know the order of energy levels for different orbitals which is shown in the figure 2.8.



Order of filling of orbitals

Figure 2.8

The order of energy levels of orbitals for H-atom is as follows :

1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < ....

The order of energy levels for the orbitals of atoms other than hydrogen (more than one electron) is as follows :

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d....

The arrangement of electrons in orbitals of atom can be given by n + l rule. If (n + l) value is same for different orbitals, the orbital with higher value of 'n' has higher energy as shown in table 2.4.

Table 2.4 Arrangement of orbitals with increasing energy on the basis of (n + l) rule.

Orbital	Value of n	Value of l	Value of (n + l)	
1s	1	0	1 + 0 = 1	
2s	2	0	2 + 0 = 2	
2p	2	1	2 + 1 = 3	2p (n = 2) has lower energy than 3s
3s	3	0	3 + 0 = 3	3s (n = 3)
3p	3	1	3 + 1 = 4	3p (n = 3) has lower energy than 4s
4s	4	0	4 + 0 = 4	4s (n = 4)
3d	3	2	3 + 2 = 5	3d (n = 3) has lower energy than 4p
4p	4	1	4 + 1 = 5	4p (n = 4)

(ii) Pauli's Exclusion Principle : The number of electrons to be filled in various orbitals is restricted by the Pauli's exclusion principle. According to this principle, all the four quantum numbers of two electrons in the same atom are not equal. This rule can also be presented in other words:

Only two electrons can remain in the same orbital with their spins opposite to each other. This principle helps in calculating the capacity of electron to be present in any subshell e.g. subshell is comprised of two electrons and thus the maximum number of electrons present in 1s subshell can be two. As there are three sub shells for p-orbital maximum six electrons can be accomodated. Similarly, d-orbital can accomodate maximum of ten electrons as it has five subshells and f-orbital can accomodate fourteen electrons as it has seven subshells.

The following table shows the arrangement of electrons.

Principal Quantam number(n)	Symbol of orbital	Orbital in orbit				No. of orbitals n^2	Total No. of electrons $2n^2$
		s	p	d	f		
1	K	1	-	-	-	1	2
2	L	1	3	-	-	4	8
3	M	1	3	5	-	9	18
4	N	1	3	5	7	16	32

(iii) Hund's Rule of Maximum Multiplicity : This rule indicates arrangement of electrons in equal energy subshell of any orbital. Subshell of some orbitals having equal energy are known as degenerate orbitals, e.g. p-orbitals have three subshells of equal energy named p_x, p_y and p_z. According to this rule, when electron enters into the orbital of equal energy subshells, they are arranged in such a way that the direction of their spins remains parallel and the value of spin quantum number remains maximum. When all the sub-shells are occupied with electrons having parallel spin attains the half filled subshell electron configuration there after pairing of electrons occur. Hund's rule can be explained by the following illustrations in table 2.5.

Table 2.5

Atomic number	Element	Electronic configuration				
		1s	2s	$2p_x$	$2p_y$	$2p_z$
5	Boron	↑↓	↑↓	↑		
6	Carbon	↑↓	↑↓	↑	↑	
7	Nitrogen	↑↓	↑↓	↑	↑	↑
8	Oxygen	↑↓	↑↓	↑↓	↑	↑
9	Fluorine	↑↓	↑↓	↑↓	↑↓	↑
10	Neon	↑↓	↑↓	↑↓	↑↓	↑↓

2.14 Stability of Half Filled and Completely Filled Orbitals

The ground state electron configuration of an element always corresponds to the state of lowest energy. Electron configuration of atoms strictly follows the three rules as studied earlier. Even though in some cases like Cr and Cu where two subshells (4s and 3d) differ slightly in their energy, then electron shifts from a subshell of lower energy (4s) to a sub-shell of higher energy (3d) provided such shift results in all orbitals of the subshells of higher energy getting either completely filled or half filled configuration and thereby attains maximum stability. Because of this electron configuration of chromium is $(Ar)3d^5\ 4s^1$ instead of $(Ar)3d^4\ 4s^2$ and electron configuration of copper is $(Ar)\ 3d^{10}\ 4s^1$ instead of $(Ar)3d^9\ 4s^2$. Such configurations will add extra stability.

$_{24}Cr$= (Ar) $3d^4$ $4s^2$

Ar	↑	↑	↑	↑		↑↓	(usual electron configuration)

$_{24}Cr$= (Ar) $3d^5$ $4s^1$

Ar	↑	↑	↑	↑	↑	↑	(more stable configuration due to half filled sub shell arrangement)

Similarly more stable configuration of copper is given as

$_{29}Cu$= (Ar) $3d^9$ $4s^2$

Ar	↑↓	↑↓	↑↓	↑↓	↑	↑↓	(usual electron configuration)

$_{29}Cu$ = (Ar) $3d^{10}$ $4s^1$

Ar	↑↓	↑↓	↑↓	↑↓	↑↓	↑	(more stable configuration due to fully filled sub shell arrangement)

We shall study about such types of abnormality later on.

SUMMARY

Atoms are constitutional species of element. They are the smallest species of element taking part in chemical reaction. In 1808, Dalton put forward the theory that atom is indivisible. Then it was discovered that atom can be divided into three fundamental particles like proton, electron and neutron.

Thomson, in 1898, presented atomic model. According to this, positive charge (proton) and negative charge (electron) are equally distributed in the surface of atom. The idea of isotopes, isobars etc. was also given. From the Rutherford's α–particle scattering experiment, it was proved that atom contains small positively charged centre called nucleus i.e. centre of atom contains positively charged protons while negatively charged electrons are arranged around the centre.

Thomson's model of an atom was not accepted because limitations exposed due to Rutherford's particle scattering experiment. Rutherford's atomic model was accepted to certain extent. Bohr gave modern model of an atom to explain some experimental phenomenon of light radiation. According to him, the total mass of an atom remains in the centre i.e. proton and neutrons are in the nucleus while electron with negligible mass rotates around the nucleus in some definite path known as an orbit. Bohr suggested that energy of the electron remains constant as far as it remains in some definite orbit. Such states are known as stable or stationary states.

Electron can go from one stable state to another one either by absorption or emission of energy. As a result spectrum is obtained. Different lines were obtained in hydrogen spectrum.

There were some defects in the Bohr's model of atom. Later on energy of orbitals, their shapes, sub-shells of orbit and spins of electron revolving around its own axis were also shown.

Thus, as a whole discovery of fundamental species of atom, theories regarding different models of atoms, modification, final model of atom were established. Explanation of orbit, orbital and electron configuration of atoms were also studied.

Position and momentum of electron cannot be measured simultaneously and precisely. Heisenberg gave uncertainty principle and de Broglie gave wave particle duality principle. The arrangement of electrons in an orbit is governed by three rules. But before this, quantum mechanics gave idea about quantized energy and four quantum numbers n, l, m, and s. Each of them has its own significance and there by electron arrangement in orbits. The three rules: Aufbau principle, Pauli's exclusion principle and Hund's rule of maximum multiplicity helped to write electron arrangement (configuration) of element. From Hund's rule stability of half filled subshells and completly filled subshells can be explained.

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) How many electrons are present in A^+ ion having eleven protons ?

(A) 11 (B) 12

(C) 10 (D) 9

(2) Which is the correct electron configuration of Na^+ ion ?

(A) [Ne] (B) [Ne] $3s^1$

(C) $1s^2\ 2s^2\ 2p^5$ (D) [Ar]

(3) Where is the zero probability of finding the electron ?

(A) Node (B) Near the nucleus

(C) Orbit (D) Antinode

(4) From which of the following it was proved that nucleus of atom contains positive charge ?

(A) Thomson's model of an atom (B) Bohr's atomic model

(C) de Broglie's principle (D) α-particle scattering experiment

(5) Which of the following is the accepted electron configuration of chromium ?

(A) [Ar]$3d^5\ 4s^1$ (B) [Ar] $4s^2\ 4p^4$

(C) [Ar] $3d^4\ 4s^2$ (D) [Ar] $4s^1\ 4p^5$

(6) Which of the following is the correct order of energy levels of atomic orbitals ?

(A) $1s < 2s < 2p < 3s < 3p$ (B) $1s < 2p < 3s < 3p < 2s$

(C) $3p < 3s < 2p < 2s < 4s$ (D) $1s < 2s < 3s < 2p < 3p$

(7) Which of the following is the relation between momentum and the wave length of moving particle according to de Broglie's principle ?

(A) Inversely proportional (B) Proportional

(C) Square root (D) No relation

(8) Which of the following is the correct formula for one Einstein ?

(A) $\dfrac{Nc}{\lambda}$ (B) $\dfrac{hc}{\lambda}$ (C) $\dfrac{Nhc}{\lambda}$ (D) $\dfrac{Nh}{\lambda c}$

(9) Which of the following is a correct pair :

(a) Aufbau principle (1) mvr

(b) Angular momentum (2) Orientation of electron in orbital

(c) Hund's rule (3) order of orbital energy

(A) b $\rightarrow$ 1 (B) a $\rightarrow$ 1 (C) c $\rightarrow$ 1 (D) b $\rightarrow$ 3

(10) Which of the following electronic configuration is not possible ?

(A) $2p^6$ (B) $3s^1$ (C) $2p^5$ (D) $3f^{12}$

(11) From which of the following equations atomic mass can be known ?

(A) Z + n (B) Z + e^- (C) N + e^- (D) Z + N

(12) How many 'nodes' are there in 3s orbital ?

(A) 3 (B) 2 (C) 1 (D) Zero.

(13) Spin multiplicity value of Nitrogen element is :

(A) 4 (B) 3 (C) 2 (D) 1.5

(14) How many subshells are associated with n = 4 ?

(A) 16 (B) 15 (C) 8 (D) 18

(15) How many unpaired electrons are present in the electron configuration of phosphorous ?

(A) 5 (B) 3 (C) 2 (D) 1

2. Write the answers of following questions in short :

(1) Explain the difference between orbit and orbital.

(2) Give the statement of de Broglie's principle.

(3) Conclusion drawn from the α–particle scattering experiment.

(4) Drawbacks of Bohr's model of an atom.

(5) Order of energy levels of atomic orbitals.

(6) Irregularities observed in the electron configuration of chromiun and copper.

(7) Importance of quantum numbers.

(8) Shapes of p and d-orbitals.

(9) What is called nodal surface ?

(10) Ground and excited state of atom.

3. Write the answers of the following questions :

(1) Absorption and Emission spectra.

(2) Spectral lines produced in atomic spectra of hydrogen.

(3) What is photon ? Write equation for energy of photon.

(4) Explain magnetic quantum number.

(5) Explain Aufbau principle.

(6) Draw the shapes of p and d-orbitals. Write the values of angular momentum quantum number ?

(7) Why spin quantum number is introduced ?

(8) Explain Heiseberg's uncertainty principle.

(9) Write a brief account of Thomson's atomic model.

(10) Position of proton, electron and neutron in atomic structure.

4. Write the answers of the following questions in detail :

(1) Explain Pauli's exclusion principle giving suitable example.

(2) Explain hydrogen spectrum.

(3) Calculate number of proton, electron and neutron in the following :

$^{32}_{16}S^{2-}$; $^{23}_{11}Na^{+}$

(4) Explain Isotope, Isobar and Isotone.

(5) Calculate wave frequency of yellow colour radiation whose wavelength is $5800\,\mathring{A}$.

(6) Calculate mass of a photon having $3.6\,\mathring{A}$ wavelength.

(7) What is the total number of orbitals associated with n = 3 ? How many electrons can be accomodated in them ?

(8) Explain by giving suitable example the stability of half filled subshell and completely filled subshell of orbital.

(9) Write Ritz's equation for the frequency of radiation. Explain each term involved in it.

(10) Calculate wavelength of electron having $2.05 \times 10^{-7}\ ms^{-1}$ velocity.