

## Chapter - 14

# Atomic Physics

The concept that matter is composed of tiny particles has been a subject of study for the philosophers from the ancient times. The author of the book Vaisheshik Darshan and Indian philosopher Maharshi Kanad considered matter as made up of tiny individual particle called parmanu. Greek philosopher Democretes also put forward a similar hypothesis. The first scientific theory about atom was given by scientist Dalton in 1803 which you have learnt in previous classes. The basic idea in all such thoughts was that atom was indivisible and it has no internal structure of its own. The experiments done towards the end of nineteenth century and in the beginning of twentieth century had put a question mark on this idea. In experiments on discharge through gases at low pressure, cathode rays were discovered which were made of negative charged particles. These particles were later on named as electrons by british scientist J.J. Thomson in 1887 considered as an essential component of all atoms. In this connection Thomson's experiment for the measurement of  $e/m$  of the electron and Millikan's oil drops experiment of electronic charge are worth mentioning. Atom is electrically neutral hence same amount of positive charge should be there in the atom as it has negative charge due to electrons. Naturally the question arose about the distribution of positive and negative charges in an atom i.e. what is the structure of atom? The same question became the basis of all propositions about atomic models. It was well established that an atom is stable, hence, in all atomic models it was essential to explain how in spite of attraction between positive and negative charges they provide stability to the atom without eliminating each other.

Apart from this it was also known in the beginning of nineteenth century that at low pressure when current flows through atomic gases or vapour or heating by a flame, the rarified gases emit electromagnetic radiations of specific frequencies which give line spectrum. In rarified gases the distances between atoms is much more, the emitted radiations are not because of mutual interaction of atoms but because of individual atoms. Every element has its characteristic spectrum. Apart from it this was also known that when metals are heated to a

high temperature they emit electrons. Up to first three decades of twentieth century efforts to provide theoretical explanation to experimental evidences became the reason for the development of different models of the atom. In this chapter first we will study about Thomson's atomic model, Rutherford's atomic model and also about their success and failure. After it we will study about Bohr's model of Hydrogen atom which in itself was a revolutionary idea. After explanation of Hydrogen spectrum by Bohr's model we will mention some of its weaknesses. In the end we will see how de Broglie's matter wave theory successfully explains postulates about orbital quantisation.

### 14.1 Thomson Model of the Atom

In 1838 Thomson proposed that an atom is positively charged sphere of radius  $10^{-10}\text{m}$ . Throughout the volume of this sphere positive charge is uniformly distributed. To balance the positive charge negative charges in the form of electrons are embedded in the sphere. In Thomson model the negative electrons are embedded in the same way as fruit pieces are kept in the pudding to increase its beauty and taste. Alternatively the arrangement of electrons is supposed to be like seeds in the water melon.

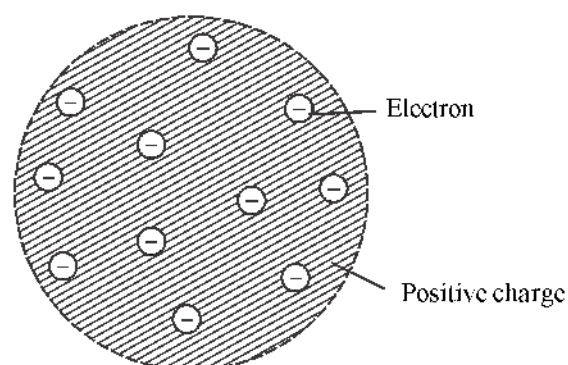


Fig 14.1 : Thomson Model

The experimental evidences till that time could be successfully explained by Thomson model. This model was able to explain successfully, stability of atom, ionisation of gases, thermionic emission of electrons. To explain emission of electromagnetic radiation from atom

Thomson supposed that after receiving energy from external sources electrons begin to oscillate about their mean positions. Because of oscillatory motion the electrons are in accelerated motion and as accelerated charge emits electromagnetic radiation hence atom emits electromagnetic radiation. Thomson assumed that frequency of radiation is the same as the frequency of oscillation of the electron. If this idea is applied to hydrogen atom which has only one electron the spectrum of hydrogen should have only one line. Experimental observations indicate there are series of spectral lines in the spectrum of hydrogen which we shall study later. In this way this model could not explain hydrogen spectrum. This model got a serious blow when this model could not explain experimental observations of Rutherford's  $\alpha$  scattering experiments.

## 14.2 Alpha Ray Scattering Experiment and Rutherford Model of Atom

In 1901 Rutherford and his associates Geiger and Marsden did an important experiment which showed that Thomson Model of atom is not correct. In this experiment  $\alpha$  rays struck a thin foil of gold and the deviated particle after passing through the foil were measured at different angles.  $\alpha$  particle is doubly ionised Helium atom whose mass is about four times the mass of hydrogen atom (7000 times the mass of electron) and has charge  $+2e$ .  $\alpha$  particles are emitted on their own by radioactive nuclei like polonium, thorium and uranium etc.

Fig 14.2 shows the experimental arrangement for  $\alpha$ -particle scattering experiment. A beam  $\alpha$ -particles from radioactive Polonium passed through lead bricks to obtain a collimated beam. This linear beam struck  $10^{-7}\text{m}$  thick foil of gold. A scintillator counter was used to detect scattered electrons at different angles. It has a screen of Zinc Sulphide which produces scintillations when  $\alpha$ -particle strike it which can be seen using a microscope and in this way the numbers of particles scattered at different angles is measured.

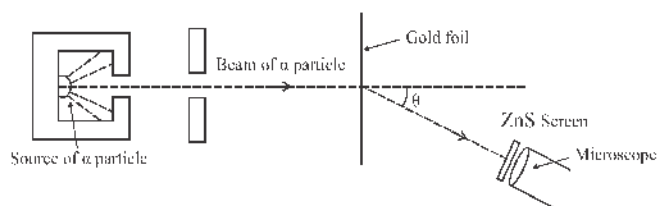


Fig 14.2 : Experimental arrangement of  $\alpha$  scattering Experiment  
Rutherford, Griger and Marden found that most of

the  $\alpha$ -particles passed through the foil undeviated or were deviated by very small angles. Rutherford concluded that the atom has lot of empty space. Hence Thomson's atomic model, which assumed atom to be uniformly distributed solid sphere, is not correct.

A more interesting result was that only a very few  $\alpha$ -particles were deflected by  $90^\circ$  or more. It was observed that one of two particles out of 8000 returned in a direction opposite to the direction of incidence. In the word of Rutherford "This is an event which I have never seen earlier in my life. It is like throwing a 15" cannon on a piece of paper which struck you back. It is impossible to explain large angle scattering by Thomson's model. Since  $\alpha$ -particles are too heavy in comparison to electron the deviation in their path due to collision with electron will be negligible. For large angle scattering of  $\alpha$ -particle it is essential that some large repelling force acts on it. In Thomson's model the positive charge is uniformly distributed in the solid sphere and hence it is not possible for a feeble positive charge to deflect  $\alpha$ -particle by a large angle. Hence there is nothing in Thomson model which can explain the returning of  $\alpha$ -particle. Rutherford argued that for a very large angle of scattering a great repulsive force should act on  $\alpha$ -particle which is possible only when all the positive charge of the atom and almost all its mass is concentrated at the centre of the atom called nucleus (instead of being distributed uniformly in the whole volume). When an  $\alpha$ -particle comes very near to the nucleus without entering into it, a large repulsive force acts on it to scatter it by a large angle.

Fig 14.3 shows the path of some  $\alpha$ -particles while crossing the atoms of gold foil. It can be easily seen that most of the  $\alpha$ -particles either do not deviate or deviate through a very small angle. Only one or two  $\alpha$ -particles that are reaching very near to nucleus are being deflected by large angle. Rutherford estimated that nucleus is of the order of  $10^{-15}$  which is  $10^5$  times shorter than the atom. For comparison, if an atom is of the size of a large stadium the nucleus is like a housefly sitting in the centre of the stadium. In this way the whole volume of atom is mostly hollow. Since the atom is mostly hollow it becomes easy to explain how an  $\alpha$ -particle comes out of the gold foil without deviation. As the thickness of the metal foil is very small it can be assumed that an  $\alpha$ -particle is not scattered more than once while crossing the foil. Since nucleus of gold is almost 50 times heavier than

an  $\alpha$  -particle it can be assumed that gold nucleus remains stationary during scattering process.

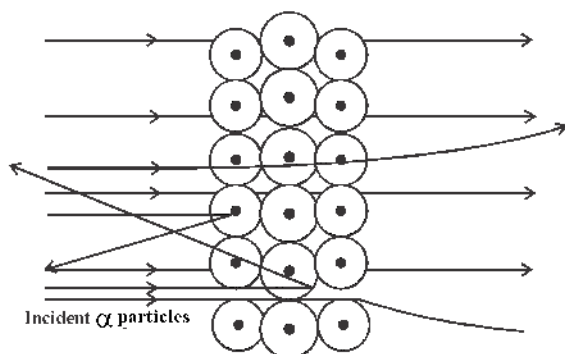


Fig 14.3 : Scattering of  $\alpha$  particles

At what angle an  $\alpha$ -particle deviates depends on how much near the centre of the atom it passes.  $\alpha$ -particle passing very near to the centre are scattered by obtuse angles. In 1911 on the basis of  $\alpha$  -particle scattering experiment Rutherford presented a new model in respect of atomic structure which is called nuclear model of atom. According to it :-

- (i) All the positive charge of the atom and nearly all the mass is confined to a very small space of  $10^{-15}$  m radius at the centre. This small space is called nucleus.
- (ii) Outside the nucleus electrons are distributed in the hollow space of radius  $10^{-10}$  m approximately. Hence most space in atom is hollow. All the positive charge in the nucleus is equal to the negative charge of electrons present in the atom.
- (iii) If the electrons were at rest they would have fallen into the nucleus due to Coulombian attraction force. Hence Rutherford assumed that electrons revolve around the nucleus and in circular paths and Coulombian attractive force provides needed centripetal force for the circular motion and only changes the direction of velocity.

In this way it is clear that Rutherford's model explain electric neutrality of atom and also hollow space in the most of the part. This model also explains emission of electrons from the atom. The nucleus is very heavy in

comparison to electrons therefore when atom gets energy from external sources nucleus is not affected.

In Rutherford model electrons were supposed to be moving in circular paths. But this motion created problems for Rutherford model. An electron moving in a circular path is accelerated and according to electromagnetic theory accelerated electron should continuously emit electromagnetic radiation. It should happen at all temperatures. Due to emission of radiation the energy of electrons will decrease continuously and the radius of its path will also decrease and the electron will move in a spiral path towards the nucleus and will ultimately fall into it, (Fig 14.4). Such an atom cannot be stable. This is failure of Rutherford model.

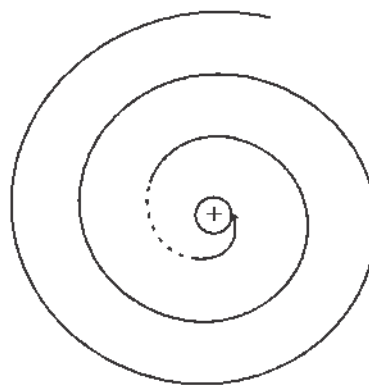


Fig 14.4 : Spiral path of electron according to Rutherford model

As mentioned above electron moving in a circular path should emit electromagnetic radiation at all temperatures the wavelength of radiation is related to frequency of revolution. Since, the radius of revolving electron is continuously decreasing the frequency of revolution should also change. Hence, an electron should emit radiations of continuously changing wavelength till it falls into the nucleus. Hence emission spectrum of the atom should be continuous. The experimental evidence is against it. The atom is not only stable but its characteristic spectrum is made up of definite wavelengths i.e. are line spectrum.

**Example 14.1 :** Find out the distance of closest approach of an  $\alpha$  -particle of energy 2.5 MeV which is being scattered by a gold nucleus (Z-79)

**Solution :** The distance of closest approach is possible only when after scattering an  $\alpha$  -particle is deviated by  $180^\circ$  and returns in the reverse direction.

This is the case of head on collision. At distance of closest approach the whole kinetic energy of  $\alpha$  -particle  $K$  equals electrical potential energy of  $\alpha$  -particle nucleus system and it comes to rest for a moment and then returns in the reverse direction due to Coulombian force of repulsion, Hence at this distance

$$K = \frac{(Ze)(2e)}{4\pi \epsilon_0 d}$$

$$\therefore d = \frac{(Ze)(2e)}{4\pi \epsilon_0 K} = \frac{2Ze^2}{4\pi \epsilon_0 K}$$

For gold nucleus  $Z=79$ ,

$$K = 2.5 \text{ MeV} = 2.5 \times 10^6 \times 1.6 \times 10^{-19} \text{ J} \\ = 4.0 \times 10^{-13} \text{ J}$$

On putting the values

$$d = \frac{2 \times 79 \times (1.6 \times 10^{-19})^2 \times 9 \times 10^9}{4.0 \times 10^{-13}} \\ = 9.10 \times 10^{-14} \text{ m}$$

### 14.3 Bohr Model for Hydrogen Atom and Hydrogen like ions

The scientist of Denmark Niel's Bohr did serious thinking about the problem of stability of atom and problem of continuous spectrum in Rutherford model. Although Bohr knew that according to classical physics electron orbits can not be stable but atom is stable. Therefore validity of widely accepted electromagnetic theory in atomic processes has to be reconsidered. It was also known at that time that for visible light, hydrogen atom cannot emit (or absorb) radiation of all wavelengths but hydrogen atom emits only 4 special wavelengths for visible light. Balmer, empirically gave a formula from which these wavelengths could be calculated.

$$\frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \text{ here } n = 3, 4, 5, 6 \dots \quad (14.1)$$

Where  $R$  is a constant later called Rydberg constant.

But neither Balmer nor anybody else could give theoretical explanation for the establishment of this formula. Bohr after seeing this formula in 1913 felt that he could explain the stability of atom and the formula provided some postulates were propounded. Bohr

mixed classical physics with early quantum concepts and put forward his theory in the form of three postulates for hydrogen atom. Initially, this theory was for hydrogen atom but it could be applicable for hydrogen like ions like  $\text{He}^+$ ,  $\text{Li}^{++}$  because in these ions only one orbital electron exists. The postulates of Bohr's theory are given below

- (i) In an atom electron revolves in some specific orbits of definite radii, while revolving in these orbits the electrons do not emit radiations (against the electromagnetic theory) These specific orbits are called stationary orbits. The centripetal force require for revolution in these orbits comes from Coulomb's attractive force.
- (ii) The second postulate of Bohr defines stationary orbits. According to it the electron can revolve only in those orbits in which its angular momentum  $L$  is a multiple of  $h/2\pi$  where  $h$  is Plank's constant. If  $n$ th orbit has a radius  $r_n$ , the velocity of electron is  $v_n$  and angular momentum is  $L_n$  then mathematically

$$L_n = m r_n v_n = n \frac{h}{2\pi} \quad \dots\dots\dots 14.2$$

Where  $n = 1, 2, 3 \dots n$  is called the principle quantum number and often  $\hbar$  is written in place of  $h/2\pi$

$$L_n = m r_n v_n = n \hbar \quad \dots (14.2(a))$$

The condition imposed by Eq. 14.2 is called Bohr's quantum condition.

- (iii) For a given stationary orbit the energy is constant. Transition of an electron from one stationary orbit to another stationary orbit can take place. If the transition of electron from high energy orbit  $E_{n_2}$  to lower energy orbit  $E_{n_1}$  takes place the frequency of emitted photon (radiation) is given by Einstein equation

$$E_{n_2} - E_{n_1} = h\nu = hc/\lambda \quad \dots (14.3)$$

The electron can absorb energy from an external source in a lower energy orbit and jump to high energy orbit.

Now we will derive expressions for radius of stationary orbit, the velocity, momentum kinetic energy and total energy of electron moving in it, according to Bohr's model.



### 14.3.1 Radius of Electron Orbits

Now, we assume that charge in the nucleus is  $Ze$  ( $Z$  is the number of protons in the nucleus and for Hydrogen  $Z=1$ ) and electron is moving at uniform speed of  $v_n$  in a circular path of radius  $r_n$  with its centre at the centre of the nucleus. For this type of motion the centripetal force is provided by the Coulombian attraction force between the nucleus and the electron i.e.

$$\frac{mv_n^2}{r_n} = \frac{Ze^2}{4\pi\epsilon_0 r_n^2} \quad \dots (14.4)$$

According to Bohr's quantum condition (eq 14.2)

$$mv_n r_n = \frac{nh}{2\pi}$$

$$\text{or} \quad v_n = \frac{nh}{2\pi m r_n} \quad \dots (14.5)$$

Putting the value of  $v_n$  from eq 14.5 in equation 14.4

$$\frac{m}{r_n} \left\{ \frac{nh}{2\pi m r_n} \right\}^2 = \frac{Ze^2}{4\pi\epsilon_0 r_n^2}$$

$$\text{or} \quad r_n = \frac{\epsilon_0 n^2 h^2}{\pi m Ze^2} \quad \dots (14.6)$$

$Ze$  for an ion similar to hydrogen is fixed  $\epsilon_0, h, \pi, m$  and  $e$  are constants hence we see that permitted radii are proportional to  $n^2$  or  $r_n \propto n^2$ . For every value of  $n$  there is a corresponding permitted orbit.

For  $n=1$  we have first orbit (minimum radius),

$n=2$  we have second orbit and so on. For Hydrogen the radius of the first orbit is given by

$$r_1 = \frac{\epsilon_0 h^2}{\pi m e^2}$$

Putting the values of other constants we have  $r_1 = 0.529 \text{ \AA} \approx 53 \text{ pm}$ . The radius of the first orbit of hydrogen is also called Bohr's radius and it is denoted by  $a_0$ . Hence

$$a_0 = \frac{h^2 \epsilon_0}{\pi m e^2} \quad \dots (14.6(a))$$

From equation (14.6) and (14.6a)

$$r_n = \frac{n^2 a_0}{Z} \quad \dots (14.7)$$

and for hydrogen

$$r_n = n^2 a_0 \quad \dots (14.7(a))$$

Hence it is clear  $r_n \propto 1/Z$  and  $r_n \propto n^2$

### 14.3.2 Orbital speed of Electron

Putting the value of  $r_n$  from equation (14.5) in equation (14.4)

$$v_n = \frac{nh}{2\pi m \left\{ \frac{\epsilon_0 n^2 h^2}{\pi m Ze^2} \right\}}$$

$$\text{or} \quad v_n = \frac{Ze^2}{2\epsilon_0 nh} \quad \dots (14.8)$$

or

$$v_n = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{n(h/2\pi)} = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{nh}$$

From equation 14.8 it is clear that  $v_n \propto Z$  and putting  $Z=1$  for  $v_n \propto 1/n$  hydrogen we get -

$$v_n = \frac{e^2}{2\epsilon_0 nh} \quad \dots (14.9)$$

and for velocity of electron in the first orbit of hydrogen atom

$$v_1 = \frac{e^2}{2\epsilon_0 h} = 2.189 \times 10^6 \text{ m/s}$$

$$\text{or} \quad v_1 = \frac{c}{137} \text{ m/s} \quad \dots (14.10)$$

Where  $c$  is the speed of light in vacuum.

**Note:** The ratio of speed of electron in first Bohr orbit ( $n=1$ ) and the speed of light in vacuum  $c$  is called fine structure constant and is denoted by  $\alpha$

$$\alpha = \frac{v_1}{c} = \frac{e^2}{2\epsilon_0 hc} = \frac{1}{137} = 7.2397 \times 10^{-3} \quad \dots (14.11)$$

### 14.3.3 Orbital frequency of Electron

Orbital frequency of electrons in  $n^{\text{th}}$  orbit (or number of revolutions per second)

$$f_n = \frac{v_n}{2\pi r_n} = \frac{1}{2\pi} \left( \frac{Ze^2}{2\epsilon_0 nh} \right) \left( \frac{\pi m Ze^2}{\epsilon_0 n^2 h^2} \right)$$

$$= \frac{mZ^2 e^4}{4\epsilon_0^2 h^3} \frac{1}{n^3} \quad \dots (14.12)$$

and the time period  $T_n = \frac{1}{f_n} = \frac{4\epsilon_0^2 h^3}{mZ^2 e^4} n^3$

clearly  $f_n \propto Z^2$  and  $f_n \propto \frac{1}{n^3}$

#### 14.3.4 Total Energy of Electron in $n^{\text{th}}$ orbit

Total energy of electron  $E_n$  is equal to the sum of its kinetic energy  $K_n$  and potential energy  $U_n$ .

$$K_n = \frac{1}{2} m v_n^2$$

$$m v_n^2 = \frac{Z e^2}{4\pi \epsilon_0 r_n}$$

$$\therefore K_n = \frac{Z e^2}{4\pi \epsilon_0 (2r_n)} \quad \dots (14.13)$$

and

$$U_n = \frac{1}{4\pi \epsilon_0} \frac{(Ze)(-e)}{r_n} = -\frac{1}{4\pi \epsilon_0} \frac{Z e^2}{r_n} \quad \dots (14.14)$$

Potential energy at infinity is Zero

Hence total energy of electron

$$E_n = K_n + U_n = \frac{1}{4\pi \epsilon_0} \frac{Z e^2}{(2r_n)} - \frac{1}{4\pi \epsilon_0} \frac{Z e^2}{r_n}$$

$$E_n = -\frac{1}{4\pi \epsilon_0} \frac{Z e^2}{2r_n} \quad \dots (14.15)$$

$$E_n = -\frac{mZ^2 e^4}{8\epsilon_0^2 h^2} \left( \frac{1}{n^2} \right) \quad \dots (14.15A)$$

From this equation it is clear that total energy of electron is quantized.

Putting the values of various constants

$$E_n = -\frac{2.18 \times 10^{-18}}{n^2} Z^2 J \quad \dots (14.16)$$

Atomic energies are generally denoted in eV instead of Joule.

Because  $1\text{eV} = 1.6 \times 10^{-19}\text{J}$  hence eq (14.16) reduces to

$$E_n = -\frac{13.6}{n^2} Z^2 \text{eV} \quad \dots (14.17)$$

For hydrogen ( $Z=1$ ) equation (14.15) to (14.17) can be written as

$$E_n = -\frac{m e^4}{8\epsilon_0 h^2 n^2} = -\frac{2.18 \times 10^{-18}}{n^2} J = -\frac{13.6}{n^2} \text{eV} \quad \dots (14.18)$$

The total energy of electron in the orbit is negative hence it shows that electron is bound to the nucleus. Hence, to eject electron from the atom energy has to be given to the electron from an external source.

For hydrogen atom and for  $n=1$  the total energy is

$$E_1 = -13.6 \text{eV}$$

Hence it can also be written that

$$E_n = -\frac{E_1}{n^2}$$

Similarly for  $n=2$

$$E_2 = \frac{E_1}{4} = -3.4 \text{eV}$$

$$\text{for orbit } n=3, E_3 = \frac{E_1}{9} = -1.5 \text{eV}$$

Fig 14.5 shows the energy levels of various stationary orbits of hydrogen. It is to be noted that total energy is negative, hence more magnitude means lower energy. The zero value is corresponding to  $n = \infty$  whose physical meaning is that distance between electron and nucleus is infinite. The minimum energy level of the atom ( $n=1$ ) is called ground level and all higher energy levels are called excited states.

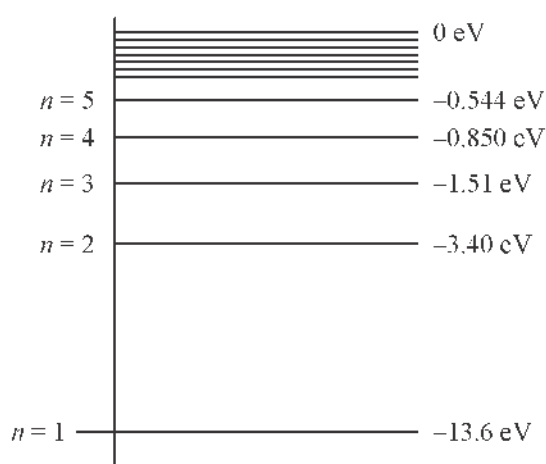


Fig 14.5 : Different energy levels for hydrogen atom

From the above discussion it is evident that  $K_n$  is always positive but  $U_n$  and  $E_n$  are always negative. Also

$$K_n = |E_n| = \frac{1}{2} |U_n|$$

Hence Kinetic energy of electron is numerically equal to magnitude of its total energy and half of the magnitude of its potential energy.

**Example 14.2 :** Find out the radius of the first orbit of  $Li$  which is similar to the atom of hydrogen.

**Solution :** For hydrogen like ions the formula for radius is

$$r_n = \frac{n^2 a_0}{Z}$$

Here Bohr radius  $a_0 = 53 \text{ pm}$

$Z=3$  for  $Li^{++}$  and for first orbit  $n=1$

$$r_1 = \frac{(1)^2 \cdot 53}{3} \text{ pm}$$

$$= 17.66 \text{ pm}$$

**Example 14.3 :** Assuming Bohr's atomic model to be true find out the expression for magnetic field of electron moving in the first orbit at the position of the nucleus of hydrogen atom in terms of fundamental constant.

**Solution :** For an electron moving in a circular path of radius  $r$  and having centre at the nucleus

$$\frac{mv^2}{r} = \frac{r^2}{4\pi\epsilon_0 r^2}$$

$$\text{or } v^2 r = \frac{e^2}{4\pi\epsilon_0 m} \dots (i)$$

For  $n=1$  according to Bohr's condition  $mvr = h/2\pi$

$$\text{or } vr = \frac{h}{2\pi m} \dots (ii)$$

from equations (i) & (ii)

$$r = \frac{\epsilon_0 h^2}{\pi m e^2} \dots (iii)$$

$$\text{and } v = \frac{e^2}{2\epsilon_0 h} \dots (iv)$$

The equivalent current for an electron moving with

speed in a circle of radius  $r$  will be  $i = \frac{ev}{2\pi r}$  such a current is like a current carrying circular loop which produces a magnetic field  $B$  at the centre.

$$B = \frac{\mu_0 i}{2r} = \frac{\mu_0 ev}{4\pi r^2}$$

Putting the values of  $v$  and  $r$  from equations (iii) and (iv)

$$B = \frac{\mu_0 e}{4\pi} \frac{e^2}{2\epsilon_0 h} \times \frac{\pi m^2 e^4}{\epsilon_0 h^2} = \frac{\mu_0 e^2 \pi m^2}{8\epsilon_0 h^3}$$

**Example 14.4 :** For an atom the energies at levels A, B and C are  $E_A$ ,  $E_B$  and  $E_C$  where  $E_A < E_B < E_C$ . If the wavelength of radiations due to transition of electrons from C to B, B to A and C to A are  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$  then prove that

$$\lambda_3 = \frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2}$$

**Solution :** We know that  $E_{n2} - E_{n1} = \frac{hc}{\lambda}$

$$\text{Hence according to Question } E_C - E_B = \frac{hc}{\lambda_1} \dots (i)$$

$$E_B - E_A = \frac{hc}{\lambda_2} \quad \dots (ii)$$

and  $E_C - E_A = \frac{hc}{\lambda_3} \quad \dots (iii)$

Adding (i) and (ii)

$$E_C - E_A = hc \left[ \frac{1}{\lambda_1} + \frac{1}{\lambda_2} \right] \quad \dots (iv)$$

Compering equations (iii) and (iv)

$$\frac{hc}{\lambda_3} = hc \left[ \frac{1}{\lambda_1} + \frac{1}{\lambda_2} \right]$$

or  $\frac{1}{\lambda_3} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$

or  $\lambda_3 = \frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2}$

**Example 14.5 :** In hydrogen atom when an electron jumps from  $n = \infty$  to  $n = 3$  what will be the wavelength of the emitted radiation?

**Solution :** For hydrogen atom  $E_n = -\frac{13.6}{n^2} eV$

$\therefore E_\infty = 0$

and  $E_3 = -\frac{13.6}{3^2} = -\frac{13.6}{9} = -1.51 eV$

Hence wavelength emitted because of transition

$$\begin{aligned} \lambda &= \frac{hc}{\Delta E} = \frac{hc}{E_\infty - E_3} \\ &= \frac{1242 eV \text{ nm}}{1.51 eV} = 822.51 \text{ nm} \end{aligned}$$

## 14.4 Line Spectrum of Hydrogen and its explanation

When hydrogen gas is filled in a sealed tube and is heated or it is filled in a tube at low pressure and current is passed through it, radiation is emitted. Radiation obtained in this way is analysed by a spectrometer and it is found that only a few specific wavelength are there. Such a spectrum is called emission line spectrum and shining lines on a black background are visible. A part of

the spectrum of atomic hydrogen gas is shown in fig 14.6

In the visible part of this spectrum four main lines can be seen and the corresponding wavelength are 656.3 nm, 486.1 nm, 434.1 nm and 410.2 nm respectively. In 1885 Swiss teacher Johan Balmer on the basis of this experiment found that wavelength of these lines and lines in the same range can be expressed by the following equation.

$$\lambda = \frac{364.56 n^2}{n^2 - 4} \quad \text{here } n = 3, 4, 5, \dots$$

The lines obtained from the above formula are expressed in nm. The series of wavelengths so obtained is called Balmer series. Some lines of Balmer series are found near ultraviolet region. After a few years the scientist called Rydberg expressed the formula of Balmer in a simpler way as follows

$$\frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \quad \text{here } n = 3, 4, 5, \dots \quad \dots (14.19)$$

Where R is a constant which is now called Rydberg constant.

If the wavelength  $\lambda$  is expressed in units of metres, then the value of R is

$$R = 1.09737 \times 10^7 \text{ m}^{-1} \approx 10^7 \text{ m}^{-1}$$

The formula of both Balmer and Rydberg were correct for wavelength of Balmer series but were not based on a theoretical model as they were formulae based on experience. On the basis of these formula it was not possible to explain the reason for the presence of specific wavelength in the line spectrum of hydrogen. It was discovered later that besides Balmer series there are other series also in the line spectrum of hydrogen which were named after their original discoverers such as Lyman series, Paschen series, Bracket series and Pfund series. In fig 14.6 Lyman series and Paschen series are also shown besides Balmer series. It can be seen that towards lower wavelength side of each series, the interval between spectral lines goes on decreasing and in the end a continuum is visible.

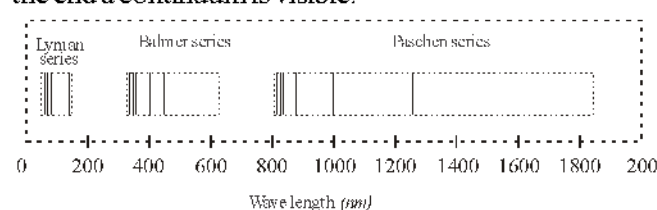


Fig 14.6



In fig 14.6 some portion of the line spectrum of hydrogen is depicted in which Lyman series, Balmer series and Paschen series are shown. The other two series, Bracket series and Pfund series which are found in far infrared region could not be shown in view of their large wavelengths.

These series can be expressed by the following formulae :-

$$\text{Lyman series } \frac{1}{\lambda} = R \left( \frac{1}{1^2} - \frac{1}{n^2} \right) n = 2, 3, 4, \dots \dots (14.20)$$

$$\text{Paschen series } \frac{1}{\lambda} = R \left( \frac{1}{3^2} - \frac{1}{n^2} \right) n = 4, 5, 6, \dots (14.21)$$

$$\text{Bracket series } \frac{1}{\lambda} = R \left( \frac{1}{4^2} - \frac{1}{n^2} \right) n = 5, 6, 7, 8, \dots (14.22)$$

$$\text{Pfund series } \frac{1}{\lambda} = R \left( \frac{1}{5^2} - \frac{1}{n^2} \right) n = 6, 7, 8, \dots \dots (14.23)$$

#### 14.4.1 Explanation of Hydrogen spectrum by Bohr's Theory

At room temperature atomic hydrogen does not emit emission spectrum because nearly all the hydrogen atoms are in their ground states ( $n=1$ ) at such temperatures and no states of lower energy are available for transition of electrons. Hence atoms do not emit radiation. When gas is given energy by heat or electric discharge or any other source, transition of electron to high energy levels  $n=2, n=3$  etc. take place. When electron returns to lower energy levels atoms emit electromagnetic radiation. According to 3<sup>rd</sup> postulate of Bohr when electron jumps from high energy level  $E_{n_2}$  to lower energy level  $E_{n_1}$ , the emitted energy is given by eqn. 14.3, which is written below

$$E_{n_2} - E_{n_1} = h\nu = \frac{hc}{\lambda}$$

$$\therefore \frac{1}{\lambda} = \frac{E_{n_2} - E_{n_1}}{hc} \dots (14.23)$$

According to Bohr's theory the total energy of electron in  $n$ th orbit is given by equation (14.15a) according to which

$$E_n = -\frac{mZ^2e^4}{8\epsilon_0^2h^3} \frac{1}{n^2}$$

$$\therefore E_{n_2} = -\frac{mZ^2e^4}{8\epsilon_0^2h^3} \frac{1}{n_2^2}$$

$$\text{and } E_{n_1} = -\frac{mZ^2e^4}{8\epsilon_0^2h^3} \frac{1}{n_1^2}$$

Putting the values of  $E_{n_2}$  and  $E_{n_1}$  in equation (14.24), we have

$$\frac{1}{\lambda} = \frac{mZ^2e^4}{8\epsilon_0^2h^3c} \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\text{or } \frac{1}{\lambda} = RZ^2 \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \dots (14.25)$$

The quantity  $\frac{1}{\lambda}$  is also called wave number and is denoted by  $\nu$

The frequency of radiation

$$\nu = \frac{c}{\lambda} = RZ^2c \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \dots (14.26)$$

$$\text{where } R = \frac{me^4}{8\epsilon_0^2h^3c} \dots (14.27)$$

is called Rydberg constant

Putting the values of constants in the expression for  $R$ , its value obtained is  $1.097373 \times 10^7 \text{ m}^{-1}$ . In terms of Rydberg constant the energy of electron in  $n$ th orbit is given by

$$E = -\frac{Rhc^2Z^2}{n^2} \dots (14.28)$$

It is useful to remember that  $Rhc = 13.6 \text{ eV}$

Many times the energy of the atom is expressed in Rydberg unit, 1 Rydberg or 1 R = -13.6 eV

For hydrogen atom ( $Z=1$ ) equation (17.25) gives

$$\frac{1}{\lambda} = R \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \dots (14.29)$$

It may be noted that in above relations  $n_2 > n_1$

If in equation (14.29)  $n_1 = 2$  and  $n_2 = n$  where  $n=3,4,5$  etc.

then we get

$$\frac{1}{\lambda} = R \left[ \frac{1}{2^2} - \frac{1}{n^2} \right] \quad n = 3, 4, 5$$

This equation is exactly the same as Balmer and Rydberg mentioned on the basis of experience. (see equation 14.19). This result is a very big achievement of Bohr's theory. In this way by putting values of  $n_1$  and  $n_2$  in equation (14.29) we can get expression for different series, eg.

$n_1 = 1$  and  $n_2 = 2, 3, 4, \dots$  we get expression for Lyman series

$n_1 = 2$  and  $n_2 = 3, 4, 5, \dots$  we get expression for Balmer series

$n_1 = 3$  and  $n_2 = 4, 5, 6, \dots$  we get expression for Paschen series

$n_1 = 4$  and  $n_2 = 5, 6, 7, \dots$  we get expression for Brackett series

$n_1 = 5$  and  $n_2 = 6, 7, 8, \dots$  we get expression for Pfund series

These have already been given by equation (14.20) to (14.23)

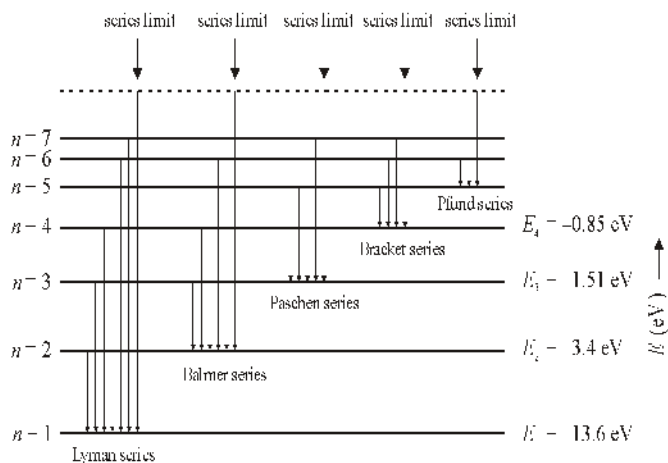


Fig 14.7 : Different energy levels and corresponding transitions for hydrogen atom for different series

Fig 14.7 shows the different energy levels and electron transitions for different series of hydrogen spectrum.

Lyman series is obtained when an electron jumps from high energy levels ( $n_2 = 2, 3, 4, \dots$ ) to ground energy state  $n_1 = 1$

In equation (14.20) putting  $n=2$  and  $n=\infty$  we

get the longest wavelength  $1216 \text{ \AA}$  and lowest wavelength  $912 \text{ \AA}$  for this series. The shortest wavelength of any series is called series limit. The limit for Lyman series is  $912 \text{ \AA}$ . Lyman series is in the ultraviolet region of electromagnetic spectrum.

For Balmer series the electron jumps from high energy levels ( $n_2 = 3, 4, 5, \dots$  etc to  $n_1 = 2$ ). This series is found in ultraviolet and visible region of electromagnetic spectrum. In this the longest wavelength is  $6563 \text{ \AA}$  and shortest wavelength series limit is  $3646 \text{ \AA}$ .

For Paschen series the transition of electron takes place from high energy levels  $n_2 = 4, 5, 6$  etc. to third energy state  $n_1 = 3$ . The lines of this series are found in infrared region of the spectrum. In this the longest wavelength is  $18751 \text{ \AA}$  and the shortest wavelength is  $8220 \text{ \AA}$ .

For Brackett series transition of electron takes place from high energy states  $n_2 = 5, 6, 7$  etc to fourth energy state  $n_1 = 4$ . These lines are also found in infrared region. The longest and the shortest wavelengths of this series are  $40477 \text{ \AA}$  and  $14572 \text{ \AA}$ , respectively

For Pfund series, transition of electron is from high energy states  $n_2 = 6, 7, 8, \dots$  etc to 5th energy state  $n_1 = 5$ . The lines of this series are also in infrared region. The longest and the shortest wavelengths are  $74515 \text{ \AA}$  and  $22768 \text{ \AA}$ , respectively.

When radiation (Photon) whose energy is just equal to energy required by an electron to take it from lower energy level fall on an atom to higher energy level then absorption of that photon takes place. If radiation of continuous frequencies after passing through a rarified gas are analysed by a spectrometer then a series of dark absorption lines in the continuous spectrum are seen which correspond to those wavelength which have been absorbed. Nearly, all the atoms of hydrogen lie in the ground state ( $n=1$ ) hence in hydrogen absorption from  $n=1$  to high energy levels is only possible.

Hence in absorption spectrum of hydrogen generally, lines of only Lyman series are present. The absorption transition of Balmer series should begin from  $n=2$  but generally there are no electrons in  $n=2$  state hence such absorption transition are not possible. Hence in absorption spectrum of hydrogen atom Balmer series as well as Paschen, Brackett and Pfund series are not present. If the temperature is too high as in the sun then

many atoms of  $n=2$  are present and their transition from  $n=2$  to higher states is possible. Thus Balmer series is present in absorption spectrum of Sun.

### 14.5 Ionisation and Excitation Potential

Generally, electrons are present in ground state in an atom but if energy is given to an atom then transition of electron to high energy levels takes place. For example, the electron in hydrogen remains in an orbit defined by principal quantum number  $n=1$  where energy is  $-13.6\text{ eV}$ . Now, if electron is given energy more than  $13.6\text{ V}$  it means total energy of electron is now positive. Actually zero total kinetic energy corresponds to that condition where separation between electron and nucleus is infinite. In such a condition electron is not bound to nucleus and is free to go anywhere. In this condition atom is ionised. The minimum energy needed to ionise an atom is called ionisation energy. The potential difference which accelerates an electron so that it receives ionisation energy is called ionisation potential. The ionisation energy for hydrogen is  $13.6\text{ eV}$  and ionisation potential is  $13.6\text{ V}$ . The energy required by an atom to go from ground state to an excited state is known as excitation energy and potential difference corresponding to it is known as excitation potential. For example the energy needed to excite a hydrogen atom from its ground state ( $n=1$ ) to first excited state, where total energy is  $-3.4\text{ eV}$ , is  $-3.4 - (-13.6) = 10.2\text{ eV}$ . This is excitation energy for orbit  $n=2$  and the excitation potential is  $10.2\text{ Volt}$ .

Bohr atomic model propounded the presence of discrete energy levels in an atom. Bohr's concept was found correct by experimental confirmation of discrete energy levels in an atom by Frank Hertz's experiment in 1904. The explanation of hydrogen spectrum given by Bohr model was very helpful in the development of modern quantum theory. For these achievements Bohr was awarded Noble Prize.

**Example 14.6 :** If initially the electron is excited in principal quantum number 3 energy level how many wavelength will be observed due to transition of electron to lower energy levels?

**Solution :** Electron present in the  $n^{\text{th}}$  state can undergo transition to  $(n-1)^{\text{th}}$ ,  $(n-2)^{\text{th}}$ , ...,  $2^{\text{nd}}$ ,  $1^{\text{st}}$  energy levels state. Thus transition from  $n^{\text{th}}$  to  $(n-1)^{\text{th}}$ ,  $(n-1)$  to  $(n-2)^{\text{th}}$  etc. is possible. Similarly transitions to lower

energy levels can be considered. Suppose  $N$  is the total number of possible transitions

$$N = (n-1) + (n-2) + (n-3) + \dots + 2 + 1$$

$$= \frac{n(n-1)}{2}$$

**Example 14.7 :** Find out the wavelength in the emitted radiations when an excited electron in  $n=4$  state returns to ground state.

**Solution :** As given in example 14.6 the total number of emitted waves, for  $n=4$

$$N = \frac{(n)(n-1)}{2} = \frac{4 \times 3}{2} = 6$$

These will be corresponding to transitions from  $n=4$  to  $n=3$ ,  $n=4$  to  $n=2$ ,  $n=4$  to  $n=1$ ,  $n=3$  to  $n=2$ ,  $n=3$  to  $n=1$  and  $n=2$  to  $n=1$

Energies for  $n=1, 2, 3$  and  $4$  are

$$E_1 = -13.6\text{ eV}$$

$$E_2 = -\frac{13.6\text{ eV}}{4} = -3.4\text{ eV}$$

$$E_3 = -\frac{13.6\text{ eV}}{9} = -1.51\text{ eV}$$

and  $E_4 = -\frac{13.6\text{ eV}}{16} = -0.85\text{ eV}$

due to transition from  $n=4$  to  $n=1$  the wavelength of emission will be

$$\lambda = \frac{hc}{\Delta E} = \frac{1242\text{ eV} \cdot \text{nm}}{(13.6 - 0.85)\text{ eV}} = 97.4\text{ nm}$$

due to transition from  $n=4$  to  $n=2$  the wavelength of emission will be

$$\lambda = \frac{hc}{\Delta E} = \frac{1242\text{ eV} \cdot \text{nm}}{(3.4 - 0.85)\text{ eV}} = 487\text{ nm}$$

due to transition from  $n=4$  to  $n=3$  the wavelength of emission will be

$$\lambda = \frac{hc}{\Delta E} = \frac{1242\text{ eV} \cdot \text{nm}}{(1.51 - 0.85)\text{ eV}} = 1881\text{ nm}$$

Similarly for transition from  $n=3$  to  $n=1$  the wavelength will be

$$\lambda = \frac{hc}{\Delta E} = \frac{1242}{(13.6 - 1.51)} \frac{eV \cdot nm}{eV} = 103 \text{ nm}$$

The wavelength obtained as a result of transition

from  $n=3$  to  $n=2$  is 654 nm

and for  $n=2$  to  $n=1$  is 122 nm

Hence different wavelengths found are 97.4 nm, 487 nm, 1881 nm, 103 nm, 654 nm and 122 nm

**Example 14.8 :** For hydrogen atom the wavelength for second line in Balmer series is 4861 Å. Find out the wavelength of 4th line in this series.

**Solution :** The comprehensive formula for wavelength of Balmer series is

$$\frac{1}{\lambda} = R \left[ \frac{1}{2^2} - \frac{1}{n^2} \right]$$

Second and fourth lines will be obtained when electron jumps from  $n=4$  and  $n=6$  to  $n=2$ . If the wavelength of corresponding lines are  $\lambda_2$  and  $\lambda_4$  respectively we have

$$\frac{1}{\lambda_2} = R \left[ \frac{1}{2^2} - \frac{1}{4^2} \right] = \frac{3}{16} R \quad \dots (i)$$

$$\frac{1}{\lambda_4} = R \left[ \frac{1}{2^2} - \frac{1}{6^2} \right] = \frac{8R}{36} \quad \dots (ii)$$

From equ (i) and (ii)

$$\frac{\lambda_4}{\lambda_2} = \frac{3R}{16} \cdot \frac{36}{8R} = \frac{27}{32}$$

$$\therefore \lambda_4 = \frac{27}{32} \times \lambda_2 = \frac{27}{82} \times 4861 \text{ Å} = 4101.5 \text{ Å}$$

**Example 14.9 :** If in the spectrum of hydrogen atom the wavelength of first line of Lyman series is 1215 Å, find out the wavelength of second line of Balmer series.

**Solution :** for first line of Lyman series the transition will be from  $n_2 = 2$  to  $n_1 = 1$

$$\frac{1}{\lambda_1} = R \left( \frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3R}{4} \quad \dots (i)$$

The transition for 2nd line of Balmer series will be from  $n_2 = 4$  to  $n_1 = 2$

Suppose its wavelength is we have  $\lambda_2'$

$$\frac{1}{\lambda_2'} = R \left( \frac{1}{2^2} - \frac{1}{4^2} \right) = \frac{3R}{16} \quad \dots (ii)$$

from equation (i) and (ii)

$$\frac{\lambda_2'}{\lambda_1} = \frac{3R}{4} \times \frac{16}{3R} = 4$$

$$\therefore \lambda_2' = 4\lambda_1 = 4 \times 1215 \text{ Å} = 4860 \text{ Å}$$

**Example 14.10 :** The wavelength of first line of Lyman series of hydrogen is equal to wavelength of second line of Balmer series of hydrogen like ion X. Calculate the energies of first two states of X.

**Solution :** For hydrogen like ion the wavelength is given by

$$\frac{1}{\lambda} = Z^2 R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

The wavelength of first line of Lyman series ( $n_1 = 1, n_2 = 2$ ) of hydrogen atom ( $Z=1$ )

The wavelength line

$$\frac{1}{\lambda_H} = R \left( \frac{1}{1^2} - \frac{1}{2^4} \right) = \frac{3}{4} R$$

According to question

$$\lambda_X = \lambda_H$$

$$\therefore \frac{3}{4} R = \frac{3}{16} Z^2 R$$

$$\text{or } Z = 2$$

This ion is ionised Helium

$$\text{Also } (E_X)_n = Z^2 (E_H)_n = 4 (E_H)_n$$

ground state of hydrogen  $n=1, E_H = -13.6$

$$\therefore (E_H)_n = -\frac{13.6}{n^2}$$

$$\text{and } (E_X)_n = -4 \frac{13.6}{n^2}$$

For first state of x

$$(E_X)_1 = -4(13.6) = -54.4 \text{ eV}$$

and for second state of x

$$(E_x)_2 = -4(13.6) = -13.6 \text{ eV}$$

**Example 14.11 :** A group of energy levels in a hydrogen like atom X wavelength are emitted due to all possible transitions. The group has energies between -0.85 eV and -0.544 eV (including these two values). Find out the atomic number of the atom (ii) calculate the minimum wavelength emitted due to these transition. (given  $hc = 1242 \text{ eV nm}$  and ground energy of hydrogen atom = -13.6 eV)

**Solution :** The energy of nth state of an atom of atomic number Z

$$E_n = -Z^2 \frac{13.6}{n^2} \text{ eV}$$

For 6 transitions four consecutive energy levels are necessary. Suppose their quantum numbers are n, n+1, n+2 and n+3 then

$$-Z^2 \frac{(13.6)}{n^2} = -0.85 \text{ eV} \quad \dots (i)$$

$$\text{and} \quad -Z^2 \frac{(13.6)}{(n+3)^2} = -0.544 \text{ eV} \quad \dots (ii)$$

Dividing eqn. (i) by eqn. (ii)

$$\frac{(n+3)^2}{n^2} = \frac{0.85}{0.544} = 1.5625$$

$$\frac{n+3}{n} = \sqrt{1.5625} = 1.25$$

hence  $n = 12$

Putting the value of n in eqn (i)

$$-Z^2 \frac{(13.6) \text{ eV}}{144} = -0.85 \text{ eV}$$

$$\text{or} \quad Z^2 = \frac{0.85 \times 144}{13.6} = 9$$

$$\text{or} \quad Z = 3$$

(ii) The wavelength emitted by transition between two energy levels having a difference  $\Delta E$  is given by

$$\lambda = \frac{hc}{\Delta E}$$

For  $\lambda$  to be minimum  $\Delta E$  should be maximum

$$\therefore (\Delta E)_{\max} = E_{n-3} - E_n = -0.544 \text{ eV} - (-0.85 \text{ eV}) = 0.306 \text{ eV}$$

$$\therefore \lambda_{\min} = \frac{hc}{(\Delta E)_{\max}} = \frac{1242 \text{ eV nm}}{0.306 \text{ eV}} = 4059 \text{ nm}$$

## 14.6 Limitations of Bohr Model

In spite of Bohr model's achievement like explanation of stability of atom and line spectrum of hydrogen it had some limitations that are described below :-

- (i) This model was valid for hydrogen and hydrogen like ions. It can not be applied to atoms having more than one electron, not even to helium. In Bohr's model there was no provision for mutual interactions of electrons in atom having more than one electron.
- (ii) In Bohr's model electrons were supposed to be moving in circular orbits but did not emit radiation even though they are in accelerated motion. For this postulate there was no theoretical explanation available in Bohr's model.
- (iii) If spectral lines of hydrogen are observed by a microscope having high resolving power it is observed that each line observed earlier is a set of many closely spaced lines. This fine structure can not be explained by Bohr's model.
- (iv) This model does not give any information about intensity of spectral lines.
- (v) This model failed to explain splitting of spectral lines due to magnetic field, (Zeeman effect) and splitting due to electric field (Stark effect).
- (vi) Generally, motion due to centripetal force is in elliptical orbits but in Bohr's model orbit are circular. It is worth mentioning that both position and momentum of electron can not be simultaneously determined accurately due to Heisenberg's uncertainty principle. In Bohr's model position and speed of electrons are simultaneously discussed.

## 14.7 Explanation of Bohr's second postulate by matter waves

According to second postulate of Bohr's theory



only those orbits are permitted in which the angular momentum of electron is quantised i.e.  $mvr = nh / 2\pi$ . As has been mentioned earlier no theoretical explanation has been given. In 1923, de Broglie on the basis of matter wave concept, proposed that in Bohr's model the electron moving in circular orbits should be treated as a matter wave and such a wave should be considered as a stationary wave for which it is essential that the circumference has integral number of wave lengths. Hence the circumference of the orbit is an integral multiple of wavelength. Mathematically, an electron moving in a circle of radius  $r$  should fulfil the following relation

$$2\pi r = n\lambda \quad n = 1, 2, \dots \quad (14.30)$$

For electron the wavelength of matter wave

$$\lambda = h / mv$$

Hence putting this value of  $\lambda$  in eq. (14.30) we have

$$2\pi r = \frac{nh}{mv}$$

or 
$$mvr = \frac{nh}{2\pi}$$

This is Bohr's second postulate.

In figure (14.8) for circular orbit,  $n=4$  a stationary wave has been shown where the circumference has four de Broglie waves. Hence  $2\pi r = 4\lambda$

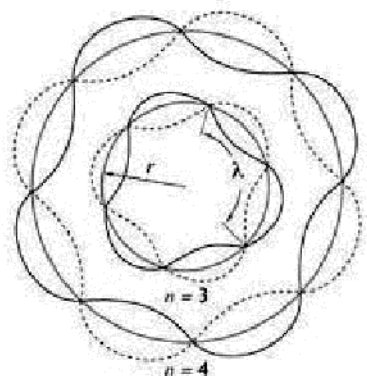


Fig. 14.8 : The stationary wave according to de Broglie principle for  $n=4$

To understand de Broglie argument in a better way let us consider the physical phenomenon of resonance. For resonance, in a specific length whole number of waves are present. For example when in a closed pipe, along the length of the pipe, should waves are spread then due to reflections at the ends of the pipe constructive interference takes place and stationary waves to high amplitude are formed and resonance occurs. In fig (14.8) if an integral number of waves are not present then after some revolutions wave will have opposite phases and will have in significant amplitude. This is the reason why de Broglie proposed an integral number of waves in the circumference (closed path)

**Example 14.12 :** The energy of hydrogen atom from ground state is  $-13.6\text{eV}$ . Calculate de Broglie wavelength of electron in this condition. For  $n=1$  find out the circumference and compare it with de-Broglie wavelength. What do you conclude from this? (given : Bohr's radius  $a = 53\text{pm}$ )

**Solution :** From Bohr's theory we know that the kinetic energy of electron  $K$  is numerically equal to its total energy.

$$K = |E|$$

Hence in first orbit the kinetic energy of electron will be  $K = 13.6\text{eV}$ . The electron gets this energy on being accelerated by  $13.6\text{eV}$ . Hence the de-Broglie wavelength of this electron

$$\lambda = \frac{12.27}{\sqrt{V}} \text{ \AA} = \frac{12.27}{\sqrt{13.6}} = 3.32 \text{ \AA}$$

Given  $a_0 = 53 \text{ pm} = 53 \times 10^{-6} \text{ m}$

Hence circumference of first orbit

$$= 2\pi a_0 = 2 \times 3.14 \times 53 \times 10^{-6} = 3.32 \text{ \AA}$$

This is equal to the wavelength of matter wave of electron. Hence in orbit  $n=1$  one full de-Broglie wave length will be present.

### Important Points

1. An atom as a whole is electrically neutral. The cathode rays obtained by discharge through gases at low pressure are actually negatively charged particles called electrons which are essential component of every atom. For electrical neutrality of atom it is necessary that it has positive charge the same amount as it has negative charge due to electrons.
2. In Thomson's atomic model an atom is supposed to be a positively charged sphere in which electrons are embedded inside it. This model could satisfactorily explain the stability of atom, ionisation of gases and thermal emission and was not able to explain the line spectrum of hydrogen. It was unsuccessful to explain the experimental observations of  $\alpha$ -particle scattering experiment of Rutherford.
3. On the basis of  $\alpha$ -particle scattering experiment Rutherford concluded that the atom has mostly empty space inside it. According to nuclear model of Rutherford the whole positive charge and nearly all mass of the atom is confined to a very small space called nucleus. Electrons revolve around it. The size of nucleus is about  $1/10000$ th of the size of the atom.
4. The main shortcomings of Rutherford's model are-
  - (i) This model can not explain stability of the atom, because electrons revolving around nucleus are in accelerated state and should emit electromagnetic radiation and should move in spiral path and ultimately fall into the nucleus.
  - (ii) This model can not explain the characteristic line spectrum of hydrogen.
5. To explain the stability and line spectrum of hydrogen atom Bohr proposed a model for hydrogen and hydrogen like ions whose three important postulates are
  - (i) In an atom the electrons revolve in definite orbits without emitting radiation. These orbits are called stationary orbits.
  - (ii) Stationary orbits are those orbits in which angular momentum of electron is an integral multiple of  $h/2\pi$ 

$$L_n = m v_n r_n = \frac{n h}{2\pi} \quad n = 1, 2, 3, \dots$$

Where  $n=1, 2, 3, \dots$  and  $n$  is called principal quantum number.
  - (iii) When an electron jumps from a stationary higher energy orbit to a lower energy orbit a photon is emitted whose energy is equal to the difference of energy levels of initial and final stationary orbits i.e.
 
$$h\nu = E_{n_2} - E_{n_1}$$

Where  $\nu$  is the frequency of emitted photon.
6. For hydrogen like atoms the radii of permitted orbits are given by
 
$$r_n = \frac{\epsilon_0 n^2 h^2}{\pi m Z e^2}$$

and energy of electrons in these orbits is given by

$$E_n = -\frac{m Z^2 e^4}{8 \epsilon_0 h^2} \left( \frac{1}{n^2} \right) = -\frac{13.6}{n^2} Z^2 \text{ (eV)}$$

For hydrogen ( $Z=1$ ) the energy of electron in ground state ( $n=1$ ) is -13.6 eV
7. For the characteristic spectrum of hydrogen, the formula for different series and corresponding wave

length are

$$(i) \quad \text{Lyman series } \frac{1}{\lambda} = R \left( \frac{1}{1^2} - \frac{1}{n^2} \right) \quad n = 2, 3, 4, \dots$$

(in ultraviolet region)

$$\lambda_{\min} = 912 \text{ \AA} \quad \lambda_{\max} = 1216 \text{ \AA}$$

$$(ii) \quad \text{Balmer series } \frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \quad n = 3, 4, 5, \dots$$

(in ultraviolet and visible region)

$$\lambda_{\min} = 3646 \text{ \AA} \quad \lambda_{\max} = 6563 \text{ \AA}$$

$$(iii) \quad \text{Paschen series } \frac{1}{\lambda} = R \left( \frac{1}{3^2} - \frac{1}{n^2} \right) \quad n = 4, 5, 6, \dots$$

$$(\text{Infrared region}) \quad \lambda_{\min} = 8107 \text{ \AA} \quad \lambda_{\max} = 18751 \text{ \AA}$$

$$(iv) \quad \text{Brackett series } \frac{1}{\lambda} = R \left( \frac{1}{4^2} - \frac{1}{n^2} \right) \quad n = 5, 6, 7, \dots$$

(Infrared region)

$$\lambda_{\min} = 14572 \text{ \AA} \quad \lambda_{\max} = 40477 \text{ \AA}$$

$$(v) \quad \text{Pfund series } \frac{1}{\lambda} = R \left( \frac{1}{5^2} - \frac{1}{n^2} \right) \quad n = 6, 7, 8, \dots$$

$$(\text{Infrared series}) \quad \lambda_{\min} = 22708 \text{ \AA} \quad \lambda_{\max} = 74515 \text{ \AA}$$

8. Bohr's model could explain line spectrum of hydrogen. For wavelength of emitted lines the comprehensive formula is

$$\frac{1}{\lambda} = R \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

Where  $n_2 > n_1$

By choosing proper value of  $n_1$  and  $n_2$  the wavelength of different lines of different series can be found.

9. Bohr's model is valid only for hydrogen like atoms. It can not be applied to even two electron atom like Helium. Even for hydrogen, this model can not explain relative intensities of different spectral lines, fine structure of spectral lines, Zeeman effect and Stark effect etc. In addition to this it does not provide any theoretical basis for second postulate also.
10. The second postulate of Bohr regarding quantisation of angular momentum can be explained on the basis of de-Broglie matter wave concept. Circular orbits correspond to stationary waves where the circumference is an integral multiple of de-Broglie wave length i.e.

$$\text{Where } 2\pi r = n\lambda \quad n = 1, 2, \dots$$

## Questions For Practice

### Multiple choice question

- The energy of hydrogen atom in ground state is  $-13.6\text{eV}$ . Its energy  $n=5$  level will be -  
(a)  $-0.5\text{eV}$  (b)  $-0.85\text{eV}$   
(c)  $-5.4\text{eV}$  (d)  $-2.7\text{eV}$
- Energy of  $n^{\text{th}}$  orbit of hydrogen atom is  $E_n = -\frac{13.6}{n^2}\text{eV}$ . The energy needed to send an electron from first orbit to second orbit will be -  
(a)  $10.2\text{eV}$  (b)  $12.1\text{eV}$   
(c)  $13.6\text{eV}$  (d)  $3.4\text{eV}$
- In hydrogen atom if an electron jumps from third to second orbit the wavelength of emitted radiation  
(a)  $\frac{5R}{36}$  (b)  $\frac{R}{6}$   
(c)  $\frac{36}{5R}$  (d)  $\frac{5}{R}$
- In which part of the electromagnetic spectrum Lyman series of hydrogen is found : -  
(a) Ultraviolet (b) Infrared  
(c) Visible (d) X-ray region
- The number of spectral lines emitted by hydrogen atom excited to  $n=4$  energy level is  
(a) 2 (b) 3 (c) 4 (d) 6
- For Lyman series of hydrogen the minimum and maximum wave lengths are  
(a)  $909\text{Å}$  and  $1212\text{Å}$   
(b)  $9091\text{Å}$  and  $12120\text{Å}$   
(c)  $303\text{Å}$  and  $404\text{Å}$   
(d)  $1000\text{Å}$  and  $3000\text{Å}$
- For some atom, when electronic transition takes place from  $2E$  to  $E$  the emitted photon's wavelength is  $\lambda$ . Wavelength of emitted photon will be when transition takes place from  $4E/3$  energy state to  $E$  energy state : -  
(a)  $\lambda/3$  (b)  $3\lambda/4$   
(c)  $4\lambda/3$  (d)  $3\lambda$
- In an excited hydrogen atom if angular momentum according to Bohr's quantum condition is  $\left(\frac{2h}{2\pi}\right)$  its energy will be -  
(a)  $-13.6\text{eV}$  (b)  $-13.4\text{eV}$   
(c)  $-3.4\text{eV}$  (d)  $-12.8\text{eV}$
- What will be the principal quantum number of the excited state from which hydrogen atom jumps to its ground state by emitting a photon of wavelength  $\lambda$   
(a)  $\sqrt{\frac{\lambda R}{\lambda R - 1}}$  (b)  $\sqrt{1 - \lambda R}$   
(c)  $\sqrt{\frac{\lambda}{\lambda R - 1}}$  (d)  $\sqrt{\frac{1 - \lambda R}{R}}$
- Which one of the following variables remains the same in all hydrogen like ions in their ground state.  
(a) orbital speed of the electron  
(b) radius of the orbit  
(c) angular momentum  
(d) energy of the atom
- The energy of a hydrogen like ion in its ground state is  $-54.4\text{eV}$  it can be  
(a)  $\text{He}^+$  (b)  $\text{Li}^{++}$   
(c)  $\text{Deuterium}^+$  (d)  $\text{Be}^{+++}$
- In a hydrogen atom on increasing the value of principal quantum number 'n' the potential energy will -  
(a) decrease (b) increase  
(c) remains the same  
(d) potential energy decreases and increases alternately
- Transition of hydrogen atom takes place from  $n=4$  to  $n=1$ , recoil momentum of hydrogen atom (in unit of  $\text{eV}/c$ ) is : -

- (a) 13.60      (b) 12.75  
(c) 0.85      (d) 22.1
14. The magnetic moment due to orbital motion of an electron in  $n^{\text{th}}$  orbit of hydrogen in term of (angular momentum =  $L$ )
- (a)  $\frac{-neI_e}{2m}$       (b)  $\frac{-eI_e}{2m}$   
(c)  $\frac{-eL}{2mn}$       (d)  $\frac{-eLm}{m}$
15. When hydrogen atom goes from ground state to first excited state the angular momentum increases by
- (a)  $6.63 \times 10^{-34} \text{ Js}$       (b)  $1.05 \times 10^{-34} \text{ Js}$   
(c)  $41.5 \times 10^{-34} \text{ Js}$       (d)  $2.11 \times 10^{-34} \text{ Js}$

#### Very short answer type questions :-

- Which experiment indicated that the whole positive charge of an atom is confined to a very minute space in the centre?
- Write two shortcomings of Rutherford model regarding structure of matter.
- In hydrogen atom if the angular momentum of electron has the value  $h/\pi$  in which orbit it is situated?
- In which region of the electromagnetic spectrum of hydrogen the Lyman series is present?
- The energy of electron in first orbit of a hydrogen like atom is -27.2 eV. What shall be its energy in third orbit?
- What is the ratio of radii of different orbits in hydrogen atom?
- What is the potential energy of electron in eV in the first orbit of hydrogen atom?
- If the radius of first Bohr orbit of hydrogen atom is 0.5 Å, write down the value of radius of fourth Bohr orbit.
- Write down the wavelength of the last line of Balmer series.
- Write down the formula for quantisation of angular momentum in Bohr's theory.
- Write down the name of the series whose few lines fall in visible region of hydrogen spectrum.

- On what hypothesis it is possible to explain second postulate of Bohr theory?

#### Short Answer type Questions :-

- Write the shortcomings of Thomson's atomic model.
- Mention the main consideration in Rutherford's atomic model.
- Explain briefly how the Rutherford atomic model is not able to explain stability of the atom.
- Write the shortcomings of Bohr's Theory.
- Hydrogen atom has only one electron but there are many lines in its emission spectrum. Explain briefly how it is possible.
- Explain how element can be identified by studying line spectra?
- In a sample of hydrogen gas most of the atoms are in  $n=1$  energy level. When visible light passes through it some spectrum lines are absorbed. Lines of which series (Lyman or Balmer) are most absorbed and why?
- According to Bohr's theory what is meant by stationary orbit and what is the condition for it?
- Balmer series was observed and analysed before other series. Can you give some reason for it?
- In Bohr model the total energy in  $n^{\text{th}}$  orbit is  $E_n$  and angular momentum is  $L_n$ . What is the relation between them?

#### Essay type Question

- Describe briefly the  $\alpha$ -particle scattering experiment of Rutherford. How was nucleus discovered by it?
- What were the shortcomings of Rutherford model? Explain in detail how Bohr removed them in his model.
- Write Bohr's postulates for hydrogen atom. Derive a formula for the total energy of the electron in  $n^{\text{th}}$  orbit.
- Explain line spectrum of hydrogen atom on the basis of Bohr's atomic model.
- Write the shortcomings of Bohr model. Explain how quantisation of orbital angular momentum



can be explained on the basis of de-Broglie matter wave theory.

6. Derive the formula for the radii of stationary orbits of hydrogen atom according to Bohr's model and prove that the radii of stationary orbits of hydrogen atom are in the ratio of 1:4:9.....

### Answers

#### Multiple type questions

1. (a) 2. (a) 3. (c) 4. (a) 5. (d) 6. (a) 7. (d)  
8. (c) 9. (a) 10. (c) 11. (b) 12. (a)  
13. (b) 14. (b) 15. (b)

#### Very short answer questions

- Rutherford  $\alpha$  particle scattering experiment
- (i) Failure to explain stability  
(ii) Failure to explain line spectrum
- second orbit
- In ultraviolet region
- 3.02 eV
- 1:4:9.....
- 27.2 eV
- $r_4 = n^2 r_1 = 16 \times 0.5 = 8.0 \text{ \AA}$
- 3048  $\text{\AA}$
- $I_n = nh/2\pi$  or  $mv_n r_n = nh/2\pi$
- Balmer series
- de-Broglie matter wave theory

#### Numerical Questions

- Find out radius of Bohr's second orbit, speed of electron in it and its total energy for hydrogen atom.  
(Given : mass of electron  $m = 9 \times 10^{-31} \text{ kg}$  ]  
 $e = 1.6 \times 10^{-19} \text{ C}$  ]  $h = 6.6 \times 10^{-34} \text{ Js}$  )  
(Ans : 2.116  $\text{\AA}$ ,  $1.1 \times 10^6 \text{ m/s}$ , -3.4 eV)
- If the wavelength of first line of Lyman series is 1216  $\text{\AA}$ . Find out the radii of first lines of Balmer and Paschen series.  
(Ans :  $\lambda_{H1} = 6566.4 \text{ \AA}$  ,  $\lambda_{P1} = 18761.1 \text{ \AA}$  )
- In an atom for transition from energy level A to C the wavelength of emitted photon is 1000  $\text{\AA}$

and for transition from B to C the photons of wavelength 5000  $\text{\AA}$  are emitted. What will be the wavelength of photon when transition from A to B energy levels?

(Ans : 1250  $\text{\AA}$ )

- Doubly ionised Lithium atom is hydrogen like whose atomic number is 3 then -  
(i) find out the wavelength of radiation required to excite an electron from first orbit to third orbit.  
(ii) how many lines will be observed in emission spectrum of the excited system?

(Ans : 114  $\text{\AA}$ , 3 lines)

- First line of Balmer series has wavelength 6564  $\text{\AA}$ , Find out Rydberg constant and wave number

(Ans :  $R = 1.097 \times 10^7 \text{ m}^{-1}$  ,  $\bar{\nu} = 15 \times 10^5 \text{ m}^{-1}$  )

- A hydrogen like ion emits radiation of frequency  $2.467 \times 10^7 \text{ Hz}$  in transition from  $n=2$  to  $n=1$ . Find the frequency of emitted radiation in transition from  $n=3$  to  $n=1$ .

(Ans :  $2.92 \times 10^7 \text{ Hz}$  )

- A monochromatic radiation of wavelength  $\lambda$  is incident on sample of hydrogen whose atoms are in ground state. Hydrogen atoms absorb the radiation and then emit waves of six different wavelengths. Find out the value of  $\lambda$  (Given :  $hc = 1242 \text{ eV.nm}$ , ground state energy of hydrogen  $E = 13.6 \text{ eV}$ )

(Ans :  $\lambda = 97.5 \text{ nm}$  )

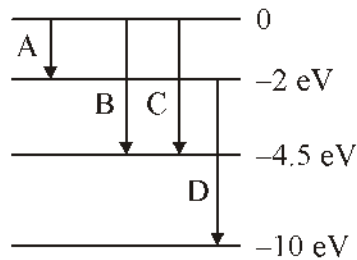
- Light corresponding to transition from  $n=4$  to  $n=2$  in hydrogen atoms incident on a metal having a work function 1.9 eV. Find out the maximum kinetic energy of emitted photo electrons.

(Ans. : 0.65 eV)

- A sample of hydrogen is in a specific excited state A. By absorption of photons of energy 2.55 eV it reaches another excited state B. Find out the principal quantum number for states A and B.

(Ans :  $n_A = 2$ ;  $n_B = 4$  )

10. The energy levels for an atom are shown in the following diagram. Find out the wavelength of photons corresponding to transitions from B and D.



(Ans : 2750Å, 1550Å)

11. For hydrogen atom find out the maximum angular speed of the electron in a stationary orbit.

(Ans :  $1.4 \times 10^{16} \text{ rad / s}$ )

12. What is the recoil momentum of hydrogen atom after emitting a photon due to transition from  $n = 5$  state to  $n = 1$  state.

(Given:  $R = 1.097 \times 10^7 \text{ m}^{-1}$

$h = 6.63 \times 10^{-34} \text{ Js}$  and mass of hydrogen

atom =  $1.67 \times 10^{-27} \text{ Kg}$ )

(Ans :  $6.98 \times 10^{-27} \text{ kg m / s}$ )