ATOMIC SPECTRA 18

BOHR'S MODEL FOR THE HYDROGEN ATOM

18.1 POSTULATES OF BOHR'S THEORY:

In order to develop a quantitative theory for the spectrum of the Hydrogen atom, Bohr in 1913 made use of plank's theory and put forward the following postulates.

(i) ***As long as electron stays in a particular orbit or stationary orbit, it neither radiates energy nor absorbs energy, i.e., total energy of electron in a particular stationary orbit remains constant.***

(ii) ***An electron can move only in those orbits in which its angular momentum "L" is integral multiple of $h/2\pi$ or $\hbar$:***

$$L = \frac{nh}{2\pi} = n\hbar \qquad \left[\frac{h}{2\pi} = \hbar\right]$$

$$\textit{OR} \qquad \boxed{mvr = n\hbar}$$

Where r is the radius of stationary orbit of electron and 'n' is the principle quantum number; n = 1, 2, 3......

(ii) ***When electron absorbs a quanta of energy '$h\upsilon$', it then jumps from lower energy level or ground state to the higher energy level or excited state, and when it falls from higher state to lower state it radiates a quanta of energy $\Delta E = h\upsilon$***

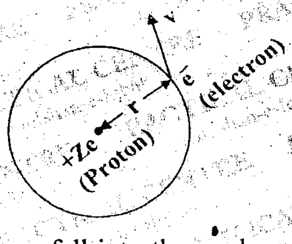
$$\Delta E = E_i - E_f$$

$$\textit{OR} \qquad h\upsilon = E_i - E_f$$

18.2 APPLICATIONS OF BOHR'S THEORY ON HYDROGEN ATOM:

In order to explain the main features of atomic model, Bohr assumed Hydrogen atom as a model. Hydrogen is the simplest of all atoms containing only one proton in its nucleus and one electron orbiting around the nucleus.

(a) Expression for the Radius of Hydrogen Atom:



The proton being massive as compared to electron and positively charged attracts the negative electron by a coulomb's force, given by:

$$F_e = \frac{Ke^2}{r^2} \quad \text{..........} (1)$$

Where 'r' is the radius of electron's orbit. May not electron fall into the nucleus, Bohr assumed that this attractive force of the proton is balanced by the centrifugal force of electron which is equal to the centripetal force given by:

$$F_c = \frac{mv^2}{r} \quad \text{........} (2)$$

Where 'v' is the velocity of electron.

Experimentally, $F_e = F_c$

from (1) & (2)

$$\frac{Ke^2}{r^2} = \frac{mv^2}{r} \quad \textit{OR} \quad \frac{Ke^2}{r} = mv^2 \quad \textit{OR} \quad V^2 = \frac{Ke^2}{mr} \quad \text{......} (3)$$

In order to determine the velocity of the electron, Bohr made use of his postulate, i.e.

$$mvr = n\hbar$$

$$\textit{OR} \qquad v = \frac{n\hbar}{mr}$$

$$\textit{OR} \qquad v^2 = \frac{n^2\hbar^2}{m^2r^2} \quad \text{........} (4)$$

From (3) & (4)

$$\frac{Ke^2}{mr} = \frac{n^2\hbar^2}{m^2r^2}$$

$$Ke^2 = \frac{n^2\hbar^2}{mr}$$

OR $$\boxed{r = \frac{n^2\hbar^2}{mKe^2}}$$

Or $$\boxed{r_n = n^2\left(\frac{\hbar^2}{mKe^2}\right)}$$

Where

$$K = \frac{1}{4\pi \epsilon_o} = \text{coulomb's constant}$$

$$\therefore \quad \boxed{r_n = n^2\left(\frac{4\pi \epsilon_o \hbar^2}{me^2}\right)}$$

Where $\frac{\hbar^2}{mKe^2}$ is a constant whose value in is 0.53 x 10^{-10}m or 0.53A° therefore.

$$\therefore \quad r_n = n^2 \text{ x } 0.53°A$$

For ground state of Hydrogen atom n = 1.

$$\therefore \quad r_1 = 0.53°A \text{ and } r_2 = 4r_1,\ r_3 = 9r_1$$

Therefore radius of nth orbit of Hydrogen atom is:

$$\therefore \quad \boxed{r_n = n^2r_1}$$

(b) Expression for the Energy of Hydrogen Atom:

The total energy of the electron orbiting around the nucleus is the sum of its potential energy (U) and Kinetic Energy (K.E).

$$E = U + K.E \quad \text{......... (1)}$$

The potential energy of the proton – electron system depends upon 'r' the radius of electron orbit. At infinite distance from nucleus, electron posses absolute potential energy which is zero. From classical theory potential energy is the negative work done at a finite distance, therefore:

$$P.E = -\text{work}$$

$$U = -\ Fd$$

OR $$U = -\frac{Ke^2}{r^2} x\cancel{r}$$

$$U = -\frac{Ke^2}{r}$$

For the Kinetic energy; equating Coloumb's attractive force between proton and electron with centripetal force of electron.

$$F_e = F_c$$

OR $$\frac{Ke^2}{\cancel{r}^2} = \frac{mv^2}{\cancel{r}}$$

$$\frac{Ke^2}{r} = mv^2$$

OR $$\frac{1}{2}\frac{Ke^2}{r} = \frac{1}{2}mv^2$$

OR $$K.E = \frac{Ke^2}{2r}$$

Eq(1) ⇒ $$E = -\frac{Ke^2}{r} + \frac{Ke^2}{2r}$$

$$\boxed{E_n = -\frac{Ke^2}{2r_n}} \quad \text{............. (2)}$$

That is the energy of electron in a particular orbit is its negative Kinetic Energy.

As $r_n = n^2 \frac{h^2}{mKe^2}$

$\therefore$ **eq(2)** $\Rightarrow$ $E_n = -Ke^2 \Big/ 2n^2 \frac{h^2}{mKe^2}$

OR $E_n = -Ke^2 \text{ x } \frac{mKe^2}{n^2h^2}$

$$\boxed{E_n = -\frac{1}{n^2}\left(\frac{mK^2e^4}{2\hbar^2}\right)}$$

$K = \frac{1}{4\pi \in}$ or $K^2 = \frac{1}{16\pi^2 \in_o^2}$

$\therefore$ $E_n = -\frac{1}{n^2}\left(\frac{me^4}{32\pi^2 \in_o^2 \hbar^2}\right)$

Where for Hydrogen atom $\frac{mK^2e^4}{2\hbar^2} = 2.18 \text{ x } 10^{-18}\text{J}$

$$= \frac{2.18\times10^{-18}}{1.6\times10^{-19}}\text{ev}$$

$$= 13.6 \text{ ev}$$

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

For n = 1 $\boxed{E_1 = -13.6\text{ev}}$ $\therefore$ $\boxed{E_n = \frac{E_1}{n^2}}$

That is, energy levels of electron are quantized.

(c) Expression of Wave Number $\left(\frac{1}{\lambda}\right)$:

Energy of stationary state of Hydrogen atom is $E_n = -\frac{1}{n^2}\left(\frac{mK^2e^4}{2\hbar^2}\right)$

Let

$$\frac{mK^2e^4}{2\hbar^2} = K'$$

$$\therefore \quad E_n = \frac{-K'}{n^2} \text{ .... (1)}$$

For higher energy level:

$$E_i = -\frac{K'}{n_i^2}$$

For lower energy level:

$$E_f = -\frac{K'}{n_f^2}$$

Energy radiated or absorbed by electron is:

$$\Delta E = E_i - E_f$$

$$\Delta E = -\frac{K'}{n_i^2} + \frac{K'}{n_f^2}$$

$$\Delta E = K' \text{ x } \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

From Bohr's theory $\Delta E = h\upsilon$

$$h\upsilon = K' \text{ x } \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

OR $$\upsilon = \frac{K'}{h} \text{ x } \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

From $c = \upsilon\lambda$

OR $$\frac{c}{\lambda} = \upsilon$$

$$\therefore \quad \frac{c}{\lambda} = \left(\frac{K'}{h}\right)\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

OR $$\frac{1}{\lambda} = \left(\frac{K'}{hc}\right)\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Where

$$\left(\frac{K'}{hc}\right) = R_H \text{ (Rydberg's Constant)}$$

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

$$\therefore \quad \boxed{\bar{\upsilon} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)} \qquad \frac{1}{\lambda} = \bar{\upsilon} = \text{Wave number}$$

Where $\bar{\upsilon}$ is the wave number of the absorbed or emitted photon. RH = 1.097×10^7/m

18.3 SPECTRUM OF HYDROGEN ATOM:

Details of atomic properties can be understood by understanding the spectral lines emitted. Due to transitions of electrons into inner shells different atoms possess different spectra. Atomic spectra of gases consisted of sharp spectral lines of definite frequencies. Some atoms have very complicated spectra. Hydrogen being the simplest one possess simple spectra which lies between visible and invisible regions.

In 1906 Lyman found a series of lines in the Hydrogen spectrum in the far ultraviolet region, known as Lyman series. In 1908 Paschan found a series in Hydrogen spectrum in the infra red region.

Similar spectral lines in invisible region were found also by P fund and Bracket. Balmer, however, found spectral lines in the visible region and also derived a formula for the wavelength of radiation as:

$$\frac{1}{\lambda} = R_H\left(\frac{1}{P^2} - \frac{1}{n^2}\right)$$

Where n_f = 1,2,3,.......... and ni = p+1, p+2, p+3,........

The various spectral series are described by the formula as:

Lyman Series

(Ultra voiletr egion) $\frac{1}{\lambda}=R_H\left(\frac{1}{1^2}-\frac{1}{n_i^2}\right)$; $n = 2, 3, 4,$..........

Balmer Series
(Visible region) $\frac{1}{\lambda}=R_H\left(\frac{1}{2^2}-\frac{1}{n_i^2}\right)$; $n = 3, 4, 5$..........

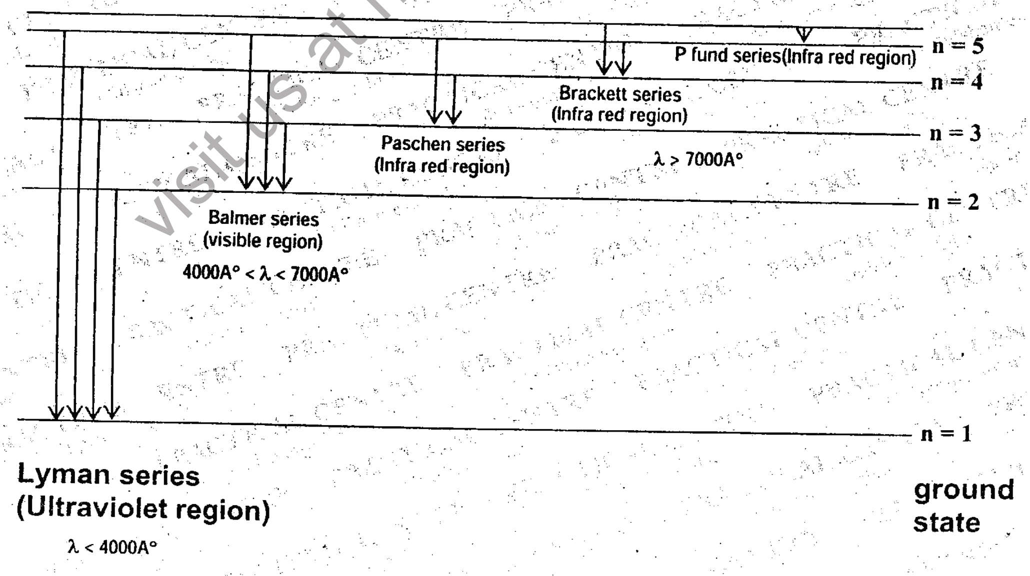
Paschen Series
(Infrared region) $\frac{1}{\lambda}=R_H\left(\frac{1}{3^2}-\frac{1}{n_i^2}\right)$; $n = 4, 5, 6$..........

Brackett Series
(Infrared region) $\frac{1}{\lambda}=R_H\left(\frac{1}{4^2}-\frac{1}{n_i^2}\right)$; $n = 5, 6, 7$..........

Pfund Series
(Infrared region) $\frac{1}{\lambda}=R_H\left(\frac{1}{5^2}-\frac{1}{n_i^2}\right)$; $n = 6, 7, 8$.........

In Balmer's Formula, the constant 'R' is called Rydberg's constant and for Hydrogen its value is:

$$R = 1.0974 \times 10^7\ m^{-1}.$$



18.4 EXCITATION AND IONIZATION POTENTIAL:

The outcome of Bohr's model is the quantization of energy of orbital electrons, i.e. electrons staying in various orbits possess different energies, that is why Bohr had assumed each orbit as energy level. The first orbit was assumed to possess the least energy called ***ground state***. The ground state electrons can reach the higher states only when electrons possess that particular sufficient energy. This process is called ***excitation of electrons***.

There are many ways of exciting electrons to different excited states, depending upon the level of states and the nature of atom. For example if the atomic gas is in an electric discharge, the electrons can be excited by applying electric field. In some of the gases, the electrons are excited by illuminating the gasses. The photons impart the energy to electron when hit with them, thus raising them to higher energy levels. Thus excitation potential is defined as ***"the accelerating potential which moves the electrons of the atom from the ground state to the higher state."***

If an electron lying in the ground state of the atom is given sufficient energy so that it is released to the orbit for which $n = \alpha$, it will disengage itself from the atom. The atom will then become positively charged it is then said to be ionized. The ionization potential is, therefore, defined to be the ***"accelerating potential which removes an electron completely from an atom."***

For Hydrogen atom ionization potential energy is 13.6eV and the corresponding ionization potential is 13.6 Volts.

18.5 X-RAY:

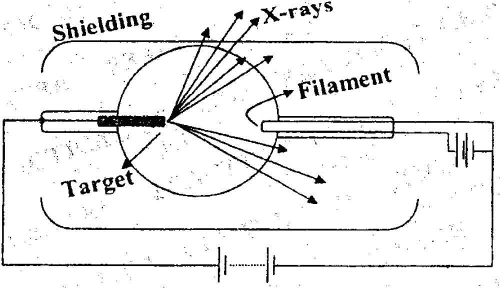
"Electromagnetic radiation having wavelength shorter than that of ultraviolet light are called X-rays". Their wave length lies in the range of 0.1nm to 1nm and frequency is of the order of 10^{18}Hz, which corresponds to quantum energies 1 KeV to 100 KeV.

Production of X-Rays:

X-rays were first observed by Rontgen in 1895 that is why they are also called as Rontgen rays. X-rays were produced by highly accelerated electrons bombarded on heavier atoms. His apparatus was consists of:

i. A source of electrons which is a Tungsten filament and serve as a cathode.
ii. A highly evacuated glass tube to accelerate the electrons.
iii. A target which serve as on anode, on which electrons strike to produce X–rays.

Rontgen observed that electrons were released when tungsten filament was heated and when they were accelerated by a thousands of voltage and allowed to hit the target of heavy atoms than a very penetrating radiation was emitted from the surface of anode. These rays were of the same nature as light or any other electromagnetic rays.



In the beginning X-rays were detected by Photographic Plates, film. But later on they could be detected by semi conductor devices also.

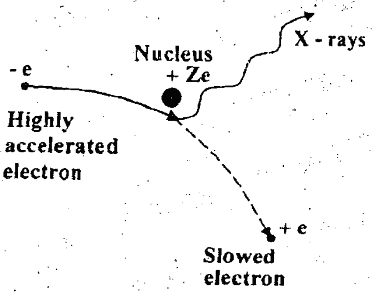
X-Rays Continuous Spectra or X-Rays Bremsstrahlung:

Spectral analysis of X-rays spectra shows a continuous spectrum when an electron accelerated through high voltage is deflected and slowed down when pass close the atomic nuclei. This spectrum is called ***Bremsstrahlung spectrum.*** According to Quantum theory when the accelerated electron is slowed down, its energy difference creates a quanta of energy $h\upsilon = E_o - E$. The process is represented as:

$$\text{Atom} + e^-(\text{fast}) \rightarrow \text{Atom} + e^-(\text{slow}) + h\upsilon.$$

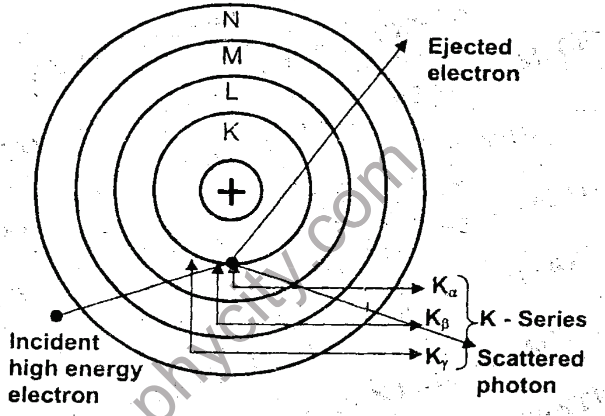
The maximum frequency or minimum wave length was observed to be always directly proportional to the accelerating voltage between the electrodes.

Further this maximum frequency was found to be very nearly independent of the material of which the electrodes are made.



Characteristic X-Rays Spectra:

In Bremsstraulung Spectra, the X-rays spectra consists of a continuous spectrum and energy distribution depend only upon the accelerating voltage. In 1913 Mosley discovered another technique of producing X-rays, in which X-rays energy depends upon the nature of target and spectrum is lined. This X-rays spectrum is called ***characteristic X-rays spectra***.



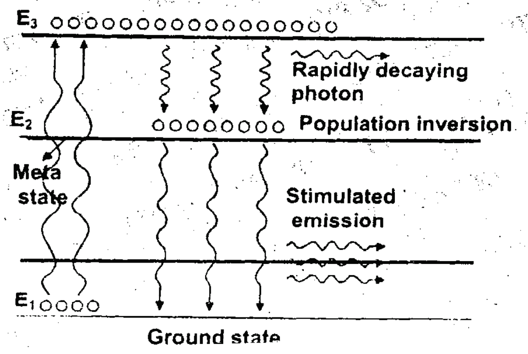
The characteristic X-rays spectra can be explained from the principle of inner shell transitions. When highly energetic electron knocks an electron from the k-shell, there occurs a vacancy in that shell, which is filled by an electron from the L shell giving up energy in the form of X-rays.

This radiation is labelled as the K_α line. The electron in the M-shell fills the vacancy in the K shell gives up energy as an X-rays called the K_β. These transitions from the shells L, M, N and so on to the K shell give rise to a series of lines K_α, K_β, K_γ and so called the K-series. Similarly when incident electrons dislodge electrons from L shell, then these transitions are called L-series.

Upon closer observation each of the characteristic X-rays line is found to be composed of a number of closely spaced lines called the X-rays fine structure.

18.6 LASER:

Lasers are one of the most important discoveries made in the second half of the twentieth century, which are now been widely used in various field. ***"The laser is a very intense, highly directional; coherent and monochromatic light beams, at frequencies from the far infrared to the ultraviolet regions."*** There are many types of lasers with power range from a milliwalt to megawatts. Basically there are four types of lasers, the solid state lasers, liquid lasers, gas lasers and semiconductor lasers.



Principle of a laser explained by considering that atoms of a material have a number of energy levels. Among which the lowest one is the ground state energy level 'E_1'. Suppose that a beam of photons of energy $\Delta E = h\upsilon$ is incident on a sample which absorbs the photons and reaches to a excited state'E_3'. This process is called ***stimulation or induced absorption***. The atoms from this state do not fall in the state 'E_1' as these transitions are not allowed. The life time of state E_3 is of the order 10^{-8} sec, therefore, transitions from this state will be spontaneous and the radiations emitted are called ***spontaneous emission*** which are of random character and incoherent. Therefore, atoms from state E_3 are allowed to decay first in the state E_2 called ***meta state*** whose life time is 10^{-3} sec. This means that the atoms reach state E_2 much faster than they leave state E_2. This results in an increased number of atoms in state E_2 as compared to the number in sate E_1. Thus ***population inversion*** is achieved. In order to sustain this process, the emitted electrons are confined in an assembly. The ends of which are fitted which mirrors. One end mirror is totally reflecting while the other is made partially reflecting for the laser to be taken cut.

RUBY LASER

Ruby is a crystal of Al_2O_3, a small number of whose Al atoms are replaced by Cr^{+++} ions, which have lost three electrons each. A high intensity helical flash lamp surrounding the ruby provides adequate pumping light to raise the Cr atoms from level E_1 to level E_3 having a short life time of the order of 10^{-8} sec. The atoms from state E_3 make transition to state E_2 with spontaneous emission making the number of atoms larger than those in state E_3. Since E_2 is a metastable state which has a life time of the order 10^{-3} sec. In this process the number 'n_1' of atoms from state E_1 are going faster to E_3 than the number n_2 of atoms leaving the state E_2. Population inversion has been created. A few Cr atoms make transitions spontaneously from level E_2 to level E_1 and these emitted photons of $\lambda = 694.3$ nm stimulate further transitions. Stimulated emission will dominate stimulated absorption because $n_2 > n_1$ and we obtain an intense coherent monochromatic red beam of light.

In practice the ruby laser is a cylindrical rod with parallel, optically reflecting ends, one of which is only partly reflecting. These emitted photons which travel exactly in the direction of the axis are reflected several times and they are capable of stimulating emission repeatedly. Those photons not in the direction of axis leave through the sides. Thus the number of photons is built up rapidly and leave through the partially transparent end of the rod.