Atomic Structure.

Bohr's Atomic Model

In 1913 a Danish Physicist Neil Bohr put forwarded a new atomic model which is based on Plank's quantum theory of radiation and some postulates of classical Physics. It explains the origin of hydrogen spectrum.

The important postulated on which the Bohr's model was based are described below.

(1) An atom consists of a dense nucleus situated at the centre with the electron revolving round it in circular orbits without emitting any energy. This orbital rotation without emitting energy (radiation) follows the Newtonian law i.e. the force of attraction between the nucleus and an electron is equal to the centrifugal force of moving electron.

(2) An electron can revolve only in those orbits whose angular momentum (mvr) is an integral multiple of (the factor) $\frac{h}{2\pi}$.

i.e. $mvr = n \cdot \frac{h}{2\pi}$

where 'm' = mass of electron, v = velocity of electron, r = Radius of orbit, n = No. of orbit in which electron is present.

(3) As long as an electron is revolving in an orbit it neither loses nor gains energy. Hence these orbits are called stationary states. Each stationary state is associated with a definite amount of energy and it is known as energy levels.

(4) An electron continues to move in a particular stationary state without losing energy. Such state of the atom is called ground state or Normal state. This is the most stable state of the atom.

(5) If energy is supplied in terms of quanta to an electron, it may jump (excite) instantaneously from a lower energy level (say 1) to a higher energy level (say 2, 3, 4, etc.) by absorbing one or more quanta of energy. This new state of electron is called the excited state.

Similarly the electron jumps from higher energy level to lower energy level by emitting one or more quanta of energy (or $h\nu$) in the form of radiation of suitable wave length.

The absorption or emission of energy takes place not as continuous waves but as small packets or bundles of discrete (separate) units of waves i.e quanta or Photons.

The energy absorbed or released in an electron jump (ΔE) is given by the following equation.

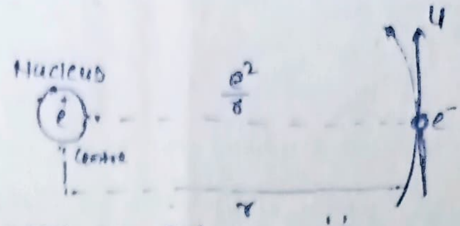
$$\Delta E = E_2 - E_1 = h\nu$$

[where h = Plank const, $h = 6.624 \cdot 10^{-34}$ J.s] & ν is frequency of radiation

Where E_1 and E_2 are the energy of electron in the first and second energy levels.

Bohr's quantum theory of Hydrogen Atom:- Working on the basis of above Postulates, Bohr was able to calculate (i) radii of the various orbits in which electron of hydrogen & hydrogen like species (having one electron i.e H, He^{+}, Li^{2+} etc) can reside and (ii) Energy of electron moving in different orbits around nucleus in Hydrogen like species

1. Calculation of radius of the Bohr's Orbit: -



let us Consider

An electron of mass m and charge 'e' revolving around a nucleus of charge Ze (where Z being the atomic number & e being the charge on Proton) with a tangential velocity u. further suppose the r is the radius of Orbit in which electron is revolving.

then by Coulomb's law, the electrostatic force of attraction (F_e) between the moving electron and nucleus is given by

$$F_e \text{ or } F_{electrostatic} = \frac{K \cdot Ze^2}{r^2} \quad \text{——— (1)}$$

where K is a Constant and its value is given by

$$K = \frac{1}{4\pi\epsilon_0}, \text{ where } \epsilon_0 \text{ is permittivity (freespace or air)}$$

$$\text{or } K = 9 \times 10^9 \ Nm^2/C^2$$

[In C.G.S the value of $K = 1$]

Now the Centrifugal force, $F_c = \frac{mu^2}{r}$ — (2)

Now, since the electrostatic force balances the Centrifugal force, for the stable electron orbit

then $F_c = F_e$

Centrifugal force = Electrostatic Force

$$\text{i.e} \quad \frac{mu^2}{r} = \frac{K Ze^2}{r^2} \quad \text{——— (3)}$$

$$\text{or} \quad u^2 = \frac{K Ze^2}{mr} \quad \text{——— (4)}$$

Now, the angular momentum of electron $= mu \cdot r$

From Bohr's Postulates

$$mur = n\left(\frac{h}{2\pi}\right) \quad \text{——— (5)}$$

where $n = 1, 2, 3$ - - etc. represents the number of Orbits (i.e energy levels)

Now from eqn (5)

$$u = \frac{nh}{2\pi mr}$$

$$\text{or} \quad u^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \quad \text{——— (6)}$$

On equating equation (4) & (6) we have

$$\frac{K \cdot Ze^2}{mr} = \frac{n^2h^2}{4\pi^2m^2r^2} \quad \text{——— (7)}$$

Solving for 'r', we get.

$$r = \frac{n^2h^2}{4\pi^2 m \cdot Ze^2 \cdot K} \quad \text{— (8)}$$

Now eqn $r = \frac{n^2 h^2}{4\pi^2 m Ze^2 K}$ enabled Bohr to Calculate the radii of the various orbits which the electron in the hydrogen atom is permitted to occupy. Evidently, the greater the value of n, i.e farther the energy level from the Nucleus, the greater is its radii.

Since for hydrogen atom, Z = 1, the above relation becomes

$$r = \frac{n^2 h^2}{4\pi^2 m e^2 K} \quad \text{i.e. eq}^n (9)$$

Hence for the radius of the first orbit, where n = 1

$$r = \frac{h^2}{4\pi^2 m e^2 K} \quad —— (10)$$

Now Putting the values,

we get,

$$r = \frac{(6.625 \times 10^{-34})^2}{4 \times (3.14)^2 \times 9 \times 10^{-31} \times (1.6 \times 10^{-19})^2 \times 9 \times 10^9}$$

$$= 5.29 \times 10^{-11} \text{ m} = 0.529 \text{ Å}$$

Thus, the radius of first orbit of hydrogen atom is 0.529 Å.

Now the radius of the first orbit of hydrogen like species is represented by r_0 and it is called Bohr's radius.

So, the Bohr's radius of hydrogen is 0.529 Å

Since radius of an orbit is directly proportional to the square of orbit number,

the radius of nth orbit for hydrogen atom can be calculated as,

$$r_n = 0.529 \times n^2 \text{ Å}$$

$$\text{or } r_n = r_0 \times n^2 \text{ Å}$$

Now we can calculate the radius of the 2nd & 3rd orbit as

Radius of 2nd Orbit, $r_2 = r_0 \times (2)^2 = r_0 \times 4 \text{ Å} = 0.529 \times 4 \text{ Å}$

$r_3 = r_0 \times (3)^2 = r_0 \times 9 \text{ Å} = 0.529 \times 9 \text{ Å}$

So we can say Radius of of 2nd orbit is four-times of 1st orbit and 3rd Orbit's radius is 9th times of the radius of 1st Orbit.

2. Calculation of velocity of electron in an orbit:-

Now the velocity with which electron is revolving in an orbit can be calculated by the relation, $u = \frac{2\pi e^2}{nh}$

Thus the velocity of electron in 1st orbit

i.e. $u = \frac{2 \times 3.14 \times (1.6 \times 10^{-19})^2}{1 \times 6.625 \times 10^{-34}} = 2.19 \times 10^8 \text{ cm sec}^{-1}$

Calculation of energy of an electron:-

The total energy of an electron revolving in a particular orbit is calculated by adding its Potential energy & Kinetic energy

$$E_{Total} = P.E. + K.E$$

The Kinetic energy of the electron $= \frac{1}{2}mu^2$

Potential energy $= -\frac{kZe^2}{r}$

Hence Total Energy $= P.E + K.E$

$$= -\frac{kZe^2}{r} + \frac{1}{2}mu^2 \quad \text{—— (11)}$$

We know, that the centrifugal force is equal to Coulombic attraction force.

So,

$$\frac{mu^2}{r} = \frac{kZe^2}{r^2}$$

$$\text{or } mu^2 = \frac{k \cdot Ze^2}{r} \quad \text{—— (12)}$$

On substituting the value of $mu^2 = \frac{KZe^2}{r}$ in equation (11)

we have,

$$E_{Total} = -\frac{KZe^2}{r} + \frac{K \cdot Ze^2}{2r}$$

$$\text{or } E_{Total} = \frac{KZe^2}{2r} - \frac{KZe^2}{r} = \frac{K \cdot Ze^2}{r}\left(\frac{1}{2} - 1\right)$$

$$= \frac{K \cdot Ze^2}{r}\left(\frac{1-2}{2}\right)$$

$$= -\frac{K \cdot Ze^2}{2r} \quad \text{—— (13)}$$

Again substituting the value of

$$r = \frac{n^2h^2}{4\pi^2 m \cdot Ze^2 \cdot K}$$

in equation (13)

$$E_{Total} = -\frac{K \cdot Ze^2}{2} \times \frac{4\pi^2 \cdot m Ze^2 \cdot K}{n^2h^2}$$

$$= -\frac{2\pi^2 Z^2 e^4 \cdot m \cdot K^2}{n^2h^2} \quad \text{—— (14)}$$

Thus the total Energy of electron in an Orbit of hydrogen atom is given by

$$E_n = -\frac{2\pi^2 Z^2 e^4 m K^2}{n^2h^2}$$

Where E_n is the total energy of electron moving in an orbit.

Calculation after putting the values.

$\pi = 3.1416$, $K = 9 \times 10^9\ Nm^2/c^2$, $e = 1.6 \times 10^{-19}\ c$, $m = 9.1085 \times 10^{-31}$ kg and $h = 6.6252 \times 10^{-34}$ joules-sec.

$$E = -\frac{21.79 \times 10^{-19}}{n^2} \text{ joules atom}^{-1}$$

$$= -\frac{21.79 \times 10^{-19}}{n^2} \times 6.2419 \times 10^{18} \text{ ev} \quad [\because 1 \text{ jule} = 6.2419 \times 10^{18} \text{ ev}]$$

$$= -\frac{13.6}{n^2} \text{ ev} = \frac{-13.6}{n^2} \times 23.053 \text{ Kcal} \quad (\because 1 \text{ ev} = 23.053 \text{ K.cal})$$

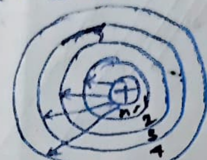
$$\text{or } E = -\frac{313.5208}{n^2} \text{ K.cal mol}^{-1}$$

where $n = 1, 2, 3 \ldots$

Origin of Hydrogen spectrum On the basis of Bohr's Theory:

When an electronic discharge is passed through hydrogen gas filled in a discharge tube at a very low pressure then the molecules of hydrogen break into atoms. Now these atoms absorb energy from the electric spark and the solitary electron (present in 1st energy level) in different atoms of hydrogen gets excited. i.e the electron shift from the energy level 1 (lowest energy level - Ground state) to different higher energy levels 2, 3, 4, etc, depending on the amount of energy absorbed by the atoms of hydrogen.

The shifting of an electron from energy level 1 (ground state) to higher energy levels, 2,3, 4,5,6,7 etc (Excited state) has been shown in fig.



These transition are represented as $1 \to 2$, $1 \to 3$, $1 \to 4$ etc respectively.

At higher energy state it is unstable and wants to come back in lower energy state for stability,

When electrons of excited state come back to lower energy level it emits energy which it has absorbed earlier in the form of Photons of light of specific frequency and hence of specific wavelength.

Thus the spectral lines of different series observed in the emission spectrum of hydrogen are due to the emission of energy photons of different wavelengths when the excited electron in hydrogen atom come back to lower energy levels, now frequency is represented by wave number - $\bar{\nu}$,

$$\bar{\nu} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] m^{-1} \quad \text{---(1)}$$

$R = 109.686 \times 10^5$

$\boxed{\nu = c/\lambda \text{ or } \frac{1}{\lambda} = \bar{\nu} \text{ (wave number)}}$ or $\frac{1}{\lambda} = \frac{\nu}{c} = \bar{\nu}$

(1). **Lyman series:** - The various spectral lines of this series is obtained when an electron jumps from the 2nd, 3rd, 4th .... Energy levels to 1st energy level. Putting $n_1 = 1$, & $n_2 = 2, 3, 4 \ldots$

(2). **Balmer series:** - Jumping of electron from 2nd, 3rd 4th 5th etc to 2nd energy level. we put $n_1 = 2$ & $n_2 = 3, 4, 5 \ldots \infty$ in eqn (1), frequencies of various spectral lines of this series is found.

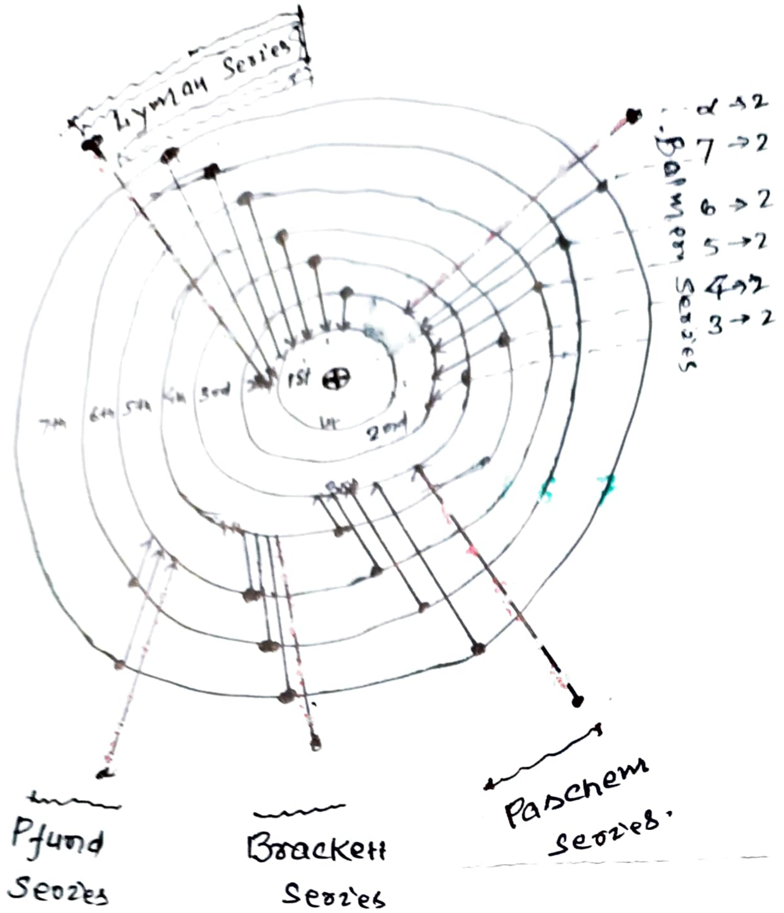
(3). **Paschen series:** Electronic jump from 4th, 5th, 6th etc. to 3rd energy level (or orbit), $n_1 = 3$, and $n_2 = 4, 5, 6 \ldots \infty$.

(4): **Brackett series:** - Electron jumps from 5th, 6th, 7th etc. to 4th energy level $n_1 = 4$ and $n_2 = 5, 6, \ldots$ etc.

(5). **Pfund series:** - When electron jumps from 6th, 7th, 8th energy levels to 5th energy level. $n_1 = 5$ and $n_2 = 6, 7, 8 \ldots \infty$

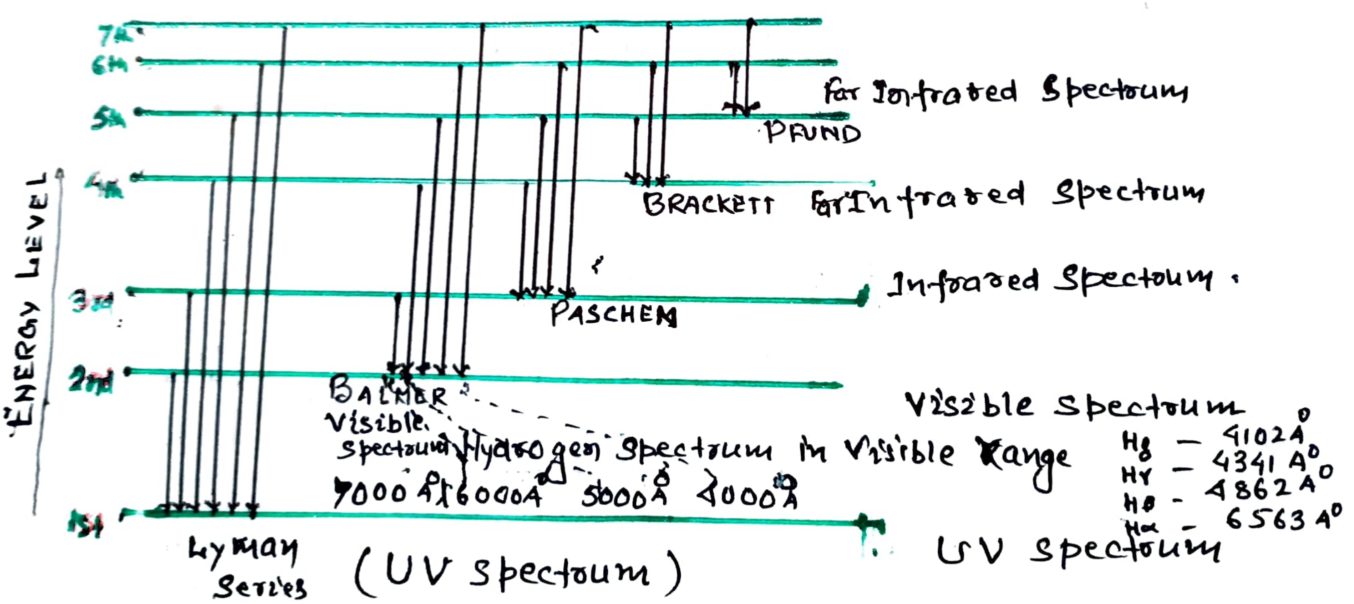
Spectrum lines	Lower energy level n_1	Higher energy level n_2	Area of spectrum
1. Lyman	1	2,3,4,5,6 ...	UV light
2. Balmer	2	3,4,5,6 ...	Visible
3. Paschen	3	4,5,6,7 ...	IR
4. Brackett	4	5,6,7,8 ...	Far IR
5. Pfund	5	6,7,8 ...	Far IR

When electron drops from higher energy level to lower, the energy released in terms of Photons of light of specific frequency and thus gives a different line in spectrum



Hδ	-	24.3×10^5
Hγ	-	23.0×10^5
Hβ	-	20.6×10^5
Hα	-	15.2×10^5

Frequency is (unit m^{-1})



The General formula to Calculate Wave Number :- $\bar{\nu} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

Where R = Rydberg Constant = $109678\ cm^{-1}$

Z = Atomic Number of Hydrogen like atom [For Hydrogen, $Z=1$]

n_1 = Number of Energy level to which an electron falls.

n_2 = Number of Energy level from which an electron falls

electron jumps from n^{th} level to ground level the No. of spectral lines = $\frac{n(n-1)}{2}$

example $n = 3$, the number of spectral lines = 3

i.e $\{(3 \rightarrow 2), (3 \rightarrow 1), \text{and } (2 \rightarrow 1)\}$