

CH-51

THE ATOMIC STRUCTURE  
OF 'H' ATOM

1. BOHR'S THEORY

Rutherford could give no satisfactory explanation of the stability of an atom. This problem was solved by Neil Bohr. He based his theory on the following postulates.

1- THE STATIONARY STATES POSTULATE:

According to this postulate electrons revolve around the nucleus in fixed orbits having definite energies. This postulate goes against the classical theory.

2- THE FREQUENCY POSTULATE:

According to this postulate an atom absorbs or emits energy only when its electron jumps up or down the fixed orbit.

If the electron jumps from high energy level  $E_n$  to lower energy level  $E_m$ . Then difference of energy is emitted in the form of a photon of energy  $h\nu_{nm}$ . Where  $\nu_{nm}$  is the frequency of radiation.

i.e., 
$$E_n - E_m = h\nu_{nm} \quad \text{--- (1)}$$

Where  $E_n$  is the energy of the electron in the  $n$ th orbit and  $E_m$  is the energy of the electron in the  $m$ th orbit and  $h\nu_{nm}$  is the energy of the photon released.

Neil Bohr then tried to explain Balmer's formula in terms of his postulates.

According to Balmer's formula.

$$\frac{1}{\lambda_{m,n}} = \left( \frac{1}{m^2} - \frac{1}{n^2} \right)$$

where  $m=2$   
Balmer Series.

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Multiplying both sides by  $hc$  we get,

$$\frac{hc}{\lambda_{m,n}} = R \left( \frac{hc}{m^2} - \frac{hc}{n^2} \right)$$

$$h\nu_{m,n} = \frac{hCR}{m^2} - \frac{hCR}{n^2} \quad \because \frac{c}{\lambda_{m,n}} = \nu_{m,n}$$

$$h\nu_{m,n} = -\frac{hCR}{n^2} + \frac{hCR}{m^2}$$

$$h\nu_{m,n} = -\frac{hCR}{n^2} - \left( -\frac{hCR}{m^2} \right) \quad \text{--- (2)}$$

Comparing (1) & (2) we get,

$$E_n - E_m = -\frac{hCR}{n^2} - \left( -\frac{hCR}{m^2} \right)$$

$$\Rightarrow E_n = -\frac{hCR}{n^2} \quad \text{--- (3)}$$

Here  $n=1, 2, 3, \dots$  for the energies of the stationary (fixed) states of H-atom.

Eq. (3) shows that energy of the electron is negative. The negative sign shows that energy has to be supplied from some external source to lift the electron to high energy level.

Sample Problem 1 Calculate the binding energy of the hydrogen atom, that is, the energy that must be added to the atom to remove the electron from its lowest energy state.

SOLUTION:

The energy required to remove the electron of H-atom is called binding energy of H-atom. It is given by,

$$\text{Binding energy of H-atom} = E_\infty - E_1$$

$$\therefore \text{Binding energy} = -\frac{hCR}{\infty} - \left( -\frac{hCR}{1^2} \right) \quad \because E_n = -\frac{hCR}{n^2}$$

$$\begin{aligned} &= 0 + hCR \\ &= hCR \\ &= 6.625 \times 10^{-34} \times 3 \times 10^8 \times 1.0974 \times 10^7 \\ &= 21.81 \times 10^{-34+8+7} \\ &= 21.81 \times 10^{-19} \text{ Joule} \\ &= \frac{21.81 \times 10^{-19}}{1.6 \times 10^{-19}} \text{ eV} \end{aligned}$$

$$\therefore \text{Binding energy} = 13.6 \text{ eV}$$

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Sample Problem 2 (a) What is the wavelength of the least energetic photon in the Balmer spectrum? (b) What is the wavelength of the series limit for the Balmer series?

SOLUTION: For Balmer series  $m=2$

(a) For wave length of least energetic photon;  $\lambda$  is max.  
 $\therefore$  For  $\lambda_{\max}$  in Balmer series.

Put  $m=2$ ,  $n=3$  in the Balmer formula

$$\frac{1}{\lambda_{\max}} = R \left( \frac{1}{m^2} - \frac{1}{n^2} \right)$$

$$= 1.097 \times 10^7 \left( \frac{1}{2^2} - \frac{1}{3^2} \right)$$

$$= 1.097 \times 10^7 \left( \frac{1}{4} - \frac{1}{9} \right)$$

$$= 1.097 \times 10^7 \left( \frac{9-4}{36} \right)$$

$$\frac{1}{\lambda_{\max}} = \frac{1.097 \times 10^7 \times 5}{36}$$

$$\therefore \lambda_{\max} = \frac{36}{1.097 \times 5 \times 10^7}$$

$$= \frac{36 \times 10^{-7}}{5.485} = 6.563 \times 10^{-7}$$

$$= 656.3 \times 10^{-9} \text{ m}$$

$$\boxed{\lambda_{\max} = 656.3 \text{ nm}}$$

(b) For wave length of series limit;  $\lambda$  is minimum.

$\therefore$  For series limit in Balmer series.

Put  $m=2$  and  $n=\infty$  in the Balmer formula.

$$\frac{1}{\lambda_{\min}} = R \left( \frac{1}{m^2} - \frac{1}{n^2} \right)$$

$$= 1.097 \times 10^7 \left( \frac{1}{2^2} - \frac{1}{\infty} \right)$$

$$\frac{1}{\lambda_{\min}} = 1.097 \times 10^7 \left( \frac{1}{4} \right)$$

$$\therefore \lambda_{\min} = \frac{4}{1.097 \times 10^7}$$

$$= \frac{4}{1.097} \times 10^{-7}$$

$$= 3.646 \times 10^{-7}$$

$$= 364.6 \times 10^{-9} \text{ m}$$

$$\boxed{\therefore \lambda_{\min} = 364.6 \text{ nm}}$$

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## DERIVATION OF THE BOHR THEORY

The atom of Hydrogen has one proton in the nucleus and an electron revolving around it. Suppose the electron is revolving in an orbit of radius  $r$  with speed  $v$ .

Let us apply Newton's II<sup>nd</sup> law of motion to the revolving electron shown in the fig.

The electron revolves around the nucleus because force of attraction of nucleus on it becomes the centripetal force.

So for the electron,

Coulomb's force = Centripetal force

$$\frac{K e \times Z e}{r^2} = m_e a_c$$

$$\therefore \frac{K e^2 Z}{r^2} = \frac{m_e v^2}{r} \quad \therefore a_c = \frac{v^2}{r}$$

$$\frac{K e^2 Z}{r} = m_e v^2$$

$$\therefore \frac{1}{4\pi\epsilon_0} \frac{Z e^2}{r} = m_e v^2 \quad \therefore K = \frac{1}{4\pi\epsilon_0}$$

$$\text{or } v^2 = \frac{1}{4\pi\epsilon_0} \frac{Z e^2}{m_e r}$$

$$v(r) = \sqrt{\frac{Z e^2}{4\pi\epsilon_0 m_e r}} \quad \text{--- (1)} \quad \therefore v = v(r)$$

As all quantities are known except  $r$ .  
So from eq. (1) we can find orbital speed of electron if  $r$  is known.

### FREQUENCY OF REVOLUTION:

As we know that,

$$v = r \omega$$

$$\therefore v = r 2\pi \nu$$

$$v = 2\pi r \nu$$

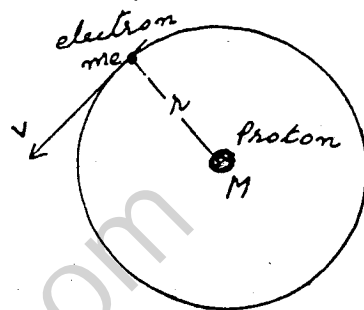
$$\therefore \nu = \frac{v}{2\pi r}$$

$$\therefore T = \frac{2\pi}{\omega}$$

$$\omega = \frac{2\pi}{T}$$

$$= 2\pi \times \frac{1}{T}$$

$$\omega = 2\pi \nu$$



Fig

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$$\nu(n) = \frac{1}{2\pi r} \times v$$

Putting the value of  $v$  from eq. (1)

$$\nu(n) = \frac{1}{2\pi r} \sqrt{\frac{Ze^2}{4\pi\epsilon_0 m_e r}}$$

$$\nu(n) = \frac{1}{\sqrt{4\pi^2 r^2}} \sqrt{\frac{Ze^2}{4\pi\epsilon_0 m_e r}}$$

$$\nu(n) = \sqrt{\frac{Ze^2}{4\pi^2 r^2 \times 4\pi\epsilon_0 m_e r}}$$

$$\nu(n) = \sqrt{\frac{Ze^2}{16\pi^3 \epsilon_0 m_e r^3}} \quad \text{--- (2)}$$

This is the expression for frequency of revolution of the orbiting electron.

### TOTAL MECHANICAL ENERGY $E(n)$

The energy of the electron in any orbit is partly K.E and partly P.E. So the total energy is given by,

$$E(n) = K(n) + U(n) \quad \text{--- (A)}$$

where  $K(n)$  is kinetic energy and  $U(n)$  is potential energy.

Now K.E is given as,

$$K(n) = \frac{1}{2} m_e v^2$$

$$\therefore K(n) = \frac{1}{2} m_e \left( \frac{Ze^2}{4\pi\epsilon_0 m_e r} \right)$$

$$\therefore v = \sqrt{\frac{Ze^2}{4\pi\epsilon_0 m_e r}}$$

$$K(n) = \frac{Ze^2}{8\pi\epsilon_0 r} \quad \text{--- (a)}$$

Now P.E is given as,

$$U(n) = P.d \times \text{charge of electron}$$

$$= \frac{kZe}{r} \times -e$$

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

$$U(n) = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}$$

$$\therefore U(n) = -\frac{Ze^2}{4\pi\epsilon_0 r} \quad \text{--- (b)}$$

$$| V = \frac{kq}{r}$$

(b)

Putting (a) and (b) in eq. (A) we get,

$$E(r) = \frac{Ze^2}{8\pi\epsilon_0 r} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

$$= \frac{Ze^2 - 2Ze^2}{8\pi\epsilon_0 r}$$

$$E(r) = -\frac{Ze^2}{8\pi\epsilon_0 r} \quad \text{--- (3)}$$

This is the expression for total energy of orbiting electron.

### ANGULAR MOMENTUM :-

The angular momentum of the revolving electron is given as,

$$L(r) = m_e v r$$

$$\therefore L(r) = m_e r \sqrt{\frac{Ze^2}{4\pi\epsilon_0 m_e r}}$$

$$= \sqrt{m_e^2 r^2 \frac{Ze^2}{4\pi\epsilon_0 m_e r}}$$

$$= \sqrt{\frac{Ze^2 m_e r}{4\pi\epsilon_0}}$$

From (1)

$$v = \sqrt{\frac{Ze^2}{4\pi\epsilon_0 m_e r}}$$

$$L(r) = \sqrt{\frac{Ze^2 m_e r}{4\pi\epsilon_0}} \quad \text{--- (4)}$$

From (1), (2), (3) and (4) we find that we can find orbital speed, the frequency of revolution, the total mechanical energy and the angular momentum if we know orbit radius.

### RELATION BETWEEN FREQUENCY AND ENERGY

If we know that the frequency of revolution of orbiting electron is,

$$\nu(r) = \sqrt{\frac{Ze^2}{16\pi^3 \epsilon_0 m_e r^3}}$$

From the equation of total energy,

$$E(r) = -\frac{Ze^2}{8\pi\epsilon_0 r}$$

$$\therefore r = -\frac{Ze^2}{8\pi\epsilon_0 E(r)}$$

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∴ The expression for frequency becomes,

$$\begin{aligned} \nu(n) &= \sqrt{\frac{Ze^2}{16\pi^3 \epsilon_0 m_e \left(-\frac{Ze^2}{8\pi \epsilon_0 E(n)}\right)^3}} \\ &= \sqrt{\frac{Ze^2 \times 8 \times 8 \times 8 \pi^3 \epsilon_0^3 E^3}{16\pi^3 \epsilon_0 m_e (-Z^3 e^6)}} \\ &= \sqrt{\frac{512 \pi^3 \epsilon_0^3 E^3 Ze^2}{16 \pi^3 m_e \epsilon_0 Z^3 e^6}} \\ &= \sqrt{\frac{32 \epsilon_0^2 E^3}{m_e Z^2 e^4}} \end{aligned}$$

$$\nu_{cm}(n) = \left( \frac{32 \epsilon_0^2 E^3}{Z^2 m_e e^4} \right)^{1/2} \quad \text{--- (5)}$$

Now we have used the subscript  $cm$  with  $\nu$ . where  $cm$  stands for classical mechanics. It means that expression (5) has been derived on the basis of classical mechanics.

Putting  $E = -\frac{hCR}{n^2}$  in the above equation (5). we get frequency calculated classically in the region of large quantum numbers.

$$\begin{aligned} \nu_{cm} &= \left[ \frac{32 \epsilon_0^2}{m_e Z^2 e^4} \left(-\frac{hCR}{n^2}\right)^3 \right]^{1/2} \\ &= \left[ \frac{32 \epsilon_0^2}{m_e Z^2 e^4} \left(-\frac{h^3 C^3 R^3}{n^6}\right) \right]^{1/2} \\ \nu_{cm} &= \left( \frac{32 \epsilon_0^2}{m_e Z^2 e^4} h^3 C^3 R^3 \right)^{1/2} \cdot \frac{1}{n^3} \quad \text{--- (6)} \end{aligned}$$

In classical physics, the frequency of revolution is equal to the frequency of emitted radiation.

∴ According to Quantum mechanics, the frequency  $\nu_{qm}$  that corresponds to classical frequency is the lowest frequency

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emitted due to transition from  $n$  to  $n-1$ .

So putting  $m = n-1$  in the eq.  $\frac{1}{\lambda} = R \left( \frac{1}{m^2} - \frac{1}{n^2} \right)$  we get,

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

$$\frac{c}{\lambda} = CR \left[ \frac{n^2 - (n-1)^2}{n^2(n-1)^2} \right]$$

$$\therefore \frac{c}{\lambda} = \nu_{qm}$$

$$\begin{aligned} \therefore \nu_{qm} &= CR \left[ \frac{n^2 - (n^2 + 1 - 2n)}{n^2(n-1)^2} \right] \\ &= CR \left[ \frac{n^2 - n^2 - 1 + 2n}{n^2(n-1)^2} \right] \end{aligned}$$

$$\nu_{qm} = \frac{CR(2n-1)}{n^2(n-1)^2} \quad \text{--- (7)}$$

This expression should agree with classical expression in the range of large quantum numbers.

When  $n \gg 1$  then eq. (7) becomes,

$$\begin{aligned} \nu_{qm} &\approx \frac{CR(2n)}{n^2(n^2)} \\ &\approx \frac{2CRn}{n^4} \end{aligned}$$

$$\nu_{qm} \approx \frac{2CR}{n^3} \quad \text{--- (8) for } n \gg 1$$

### EXPRESSION FOR RYDBERG CONSTANT

According to correspondence principle the quantum frequency  $\nu_{qm}$  should be equal to the classical frequency  $\nu_{cm}$  for large quantum numbers, i.e.,

$$\nu_{qm} = \nu_{cm}$$

$\therefore$  Equating (6) and (8) we get,

$$\frac{2CR}{n^3} = \left( \frac{32E_0^2 h^3 c^3 R^3}{m_e Z^2 e^4} \right)^{1/2} \cdot \frac{1}{n^3}$$



Squaring both sides we get,

$$4C^2R^2 = \frac{32E_0^2 h^3 C R}{m_e Z^2 e^4}$$

$$1 = \frac{8E_0^2 h^3 C R}{m_e Z^2 e^4}$$

$$R = \frac{m_e Z^2 e^4}{8E_0^2 h^3 C} \quad \text{--- (9)}$$

This is the expression for Rydberg constant.

## QUANTUM EXPRESSION FOR ENERGY ( $E_n$ )

As  $E_n = -\frac{hCR}{n^2}$

Putting the value of R from (9) we get,

$$E_n = -\frac{hc}{n^2} \left( \frac{m_e Z^2 e^4}{8E_0^2 h^3 C} \right)$$

$$E_n = -\frac{m_e Z^2 e^4}{8E_0^2 h^2} \cdot \frac{1}{n^2} \quad \text{--- (10)}$$

This is quantum expression for energy of the stationary states of H-atom.

## EXPRESSION FOR RADII OF BOHR'S

### QUANTIZED ORBITS

As the total mechanical energy of electron is given -

$$E_n = -\frac{Ze^2}{8\pi\epsilon_0 r_n}$$

So  $E_n = E_n$

$$\therefore -\frac{Ze^2}{8\pi\epsilon_0 r_n} = -\frac{m_e Z^2 e^4}{8E_0^2 h^2} \cdot \frac{1}{n^2}$$

$$\therefore r_n = -\frac{8E_0^2 h^2 n^2}{m_e Z^2 e^4} \times \frac{Ze^2}{8\pi\epsilon_0}$$

$$\therefore r_n = \left( \frac{E_0 h^2}{Z e^2 \pi m_e} \right) n^2$$

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$$r_n = a_0 n^2 \quad \text{--- (11)}$$

where  $a_0 = \frac{\epsilon_0 h^2}{2e^2 \pi^2 m_e}$

$a_0$  is called radius of Bohr orbit for  $n=1$   
Its value is,

$$\begin{aligned} a_0 &= \frac{\epsilon_0 h^2}{2e^2 \pi^2 m_e} \\ &= \frac{8.85 \times 10^{-12} \times (6.625 \times 10^{-34})^2}{1 \times (1.6 \times 10^{-19})^2 \times 3.14 \times 9.1 \times 10^{-31}} \\ &= \frac{8.85 \times 6.625 \times 6.625 \times 10^{-80}}{2.56 \times 3.14 \times 9.1 \times 10^{-69}} \\ &= 5.3 \times 10^{-11} \\ &= 0.53 \times 10^{-10} \text{ m} \end{aligned}$$

$$a_0 = 0.53 \text{ \AA}$$

The quantization of energy by equation (10) and radius by equation (11) imply that other mechanical properties are also quantised.

## BOHR'S QUANTIZATION RULE AND DE-BROGLIE WAVE

According to Bohr's quantization rule of angular momentum.

$$L_n = n \left( \frac{h}{2\pi} \right)$$

$$L_n = n \hbar$$

where  $\hbar = \frac{h}{2\pi}$

Bohr gave no justification for this quantization rule. However, this rule was proved later on by de-Broglie.

According to de-Broglie if orbiting electron is represented in terms of de-Broglie wave. Then only those orbits are possible whose circumference is equal to integral multiple of de-Broglie's wave length associated with the orbiting electron.

i.e.,  $2\pi r = n\lambda$

As de Broglie's wave length is  $n = 1, 2, 3, \dots$

$$\lambda = \frac{h}{p}$$

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$$\therefore 2\pi r = n \frac{h}{p}$$

$$p r = \frac{n h}{2\pi} \quad \therefore p r = L_n$$

$$\therefore L_n = \frac{n h}{2\pi}$$

$$L_n = n \hbar$$

Which is Bohr's quantization rule.  
The Bohr orbit and de Broglie's wave is shown in the figure.

#### 4- BOHR'S THEORY OF CRITICAL POTENTIALS AND FRANK-HERTZ EXPERIMENT

### Bohr's Theory of Critical Potentials

According to Bohr's theory, an atom can be excited or ionized by supplying energy to it by different sources.

One method of exciting the atom is to bombard it with some outside electron accelerated by an electric field. The K.E of the electron depends upon the potential difference  $V$  of the electric field and is given by,

$$K_e = \frac{1}{2} m v^2$$

As long as the value of accelerating potential is less than a certain value called CRITICAL POTENTIAL, the bombarding electron does not lose any energy and bounces back, then the collision is elastic. So the electron bounces back after the collision because the atom does not absorb any energy.

But when the value of accelerating potential is greater than CRITICAL POTENTIAL then the bombarding electron transfers its energy to the atom and the atom is excited or ionized. Now the collision is elastic because

atom has absorbed some energy. The critical potential (accelerating pot.) which excites an atom by lifting its electron from its ground state to any high energy state is called "EXCITATION POTENTIAL". So the excitation potential is that value of critical potential which excites an atom from its normal state to any high energy state. The excitation potential is also called radiation potential because atom emits radiation during deexcitation. The excitation potential is also called resonance potential because the atom can also be excited by light radiation.

If the critical potential (accelerating potential) is such that it lifts the electron of the atom from its ground state to the state at infinity, then it is called "IONIZATION POTENTIAL". So ionization potential is that value of critical potential which removes an electron from the atom.

So we find that critical potential may be excitation potential or ionization potential. Also the excitation potential is always less than ionization potential, because an atom possesses highest value of energy in the ionized state.

Suppose an electron accelerated through a potential difference 'V' collides with an atom and lifts an electron in it from inner mth state to some outer nth state. Then we have,

$$Ve = E_n - E_m$$

$$V = \frac{E_n - E_m}{e} \quad \text{--- (A)}$$

Where V is called critical potential.

However, if  $m=1$ , then  $V = \frac{E_n - E_1}{e}$  is called excitation pot.

If  $m=1$  and  $n=\infty$ , then  $V = \frac{E_\infty - E_1}{e}$  is called ionization pot.

An atom can have a number of excitation potentials but a limited number of ionization potentials. e.g, Hydrogen has only one ionization potential 13.6 volts but a number of excitation potentials.

The atoms with more than one electrons can have more than one ionization potential called 1st, 2nd ionization potentials.

e.g. He has two ionization potentials 24.5 volts and 78.6 volt.

If the bombarding electron transfers its entire energy to the atom with which it collides, then the critical potential can be used to measure the wave length of radiation emitted by the atom during de-excitation.

If  $V$  is the critical potential and  $\lambda$  the wave length of the emitted radiation, then,

$$Ve = h\nu \quad \therefore \nu = \frac{c}{\lambda}$$

$$Ve = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{Ve}$$

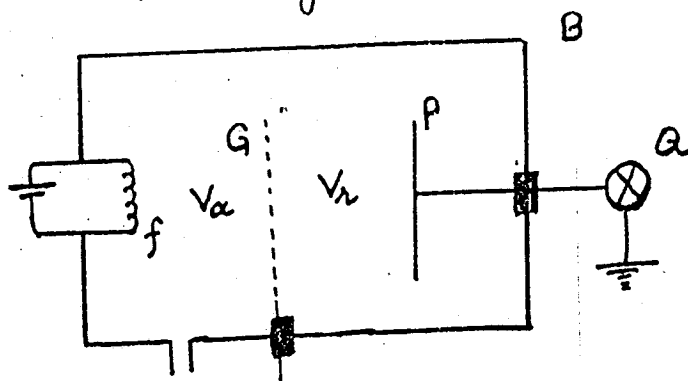
## Frank Hertz Experiment

Bohr's theory of critical potentials has been verified by FRANK and HERTZ experimentally. In 1914 Frank and Hertz measured the critical potentials and gave a proof of existence of discrete energy levels in atoms.

Fig shows the experimental arrangement of Frank and Hertz for measuring critical potentials. The box B contains monoatomic vapours e.g. Hg at a suitable low pressure.

Electrons emitted by the hot filament 'f' are accelerated by a potential difference 'Va' applied between the filament 'f' and the grid 'G'. The value of Va can be changed. A retarding potential 'Vs' of about  $\frac{1}{2}$  volt is applied between the grid 'G' and plate P i.e., G is made +ve w.r.t plate P, so that the electrons between G and P are pulled from P to G. Hence only that electron passing through 'G' will reach the plate 'P' whose energy is greater than  $\frac{1}{2}$  eV.

If 'Va' is gradually increased, the number of electrons reaching 'P' goes on increasing. The quadrant



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electrometer 'Q' measures the charge received by P. The rate of increase of charge gives the current.

As  $V_a$  is increased, the current also increases but there is a sudden fall in current when  $V_a = 4.9$  volts.

The reason of this fall is that at  $V_a = 4.9$  volts, the electrons now lose their energy to excite the atoms of Hg and so the energy of the electrons is consumed in exciting the Hg atoms due to inelastic collisions. So the electrons of Hg atoms to 1st excited state. So electrons lose all their energy before reaching the grid 'G'. Hence a retarding potential of  $\frac{1}{2}$  volt is enough to prevent them from reaching the plate 'P'. So we get a sudden fall in the value of current.

When ' $V_a$ ' is increased beyond 4.9 volts, the current begins to increase again because electrons gain enough energy to reach plate P. When  $V_a$  reaches  $2 \times 4.9 = 9.8$  volts, the current falls again because the electrons now make inelastic collisions with Hg atoms to raise them to the next excited state. Similarly at  $V_a = 3 \times 4.9 = 14.7$  volts, the current falls again. So 4.9 volt is a critical potential for Hg. In case of Hg 18 critical potentials have been observed. Their values have also been calculated from the frequencies of spectral lines emitted by Hg atoms during deexcitation to their normal state. Similar results are obtained with other elements. Thus verifying Bohr's theory of critical potentials expressed by eq. (A)

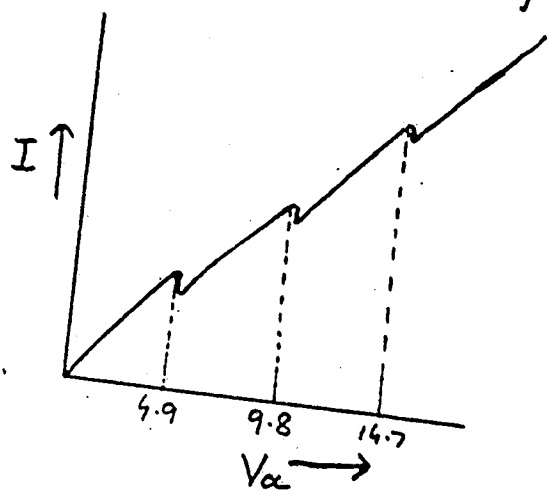


Fig shows a graph between  $V_a$  and  $I$ .

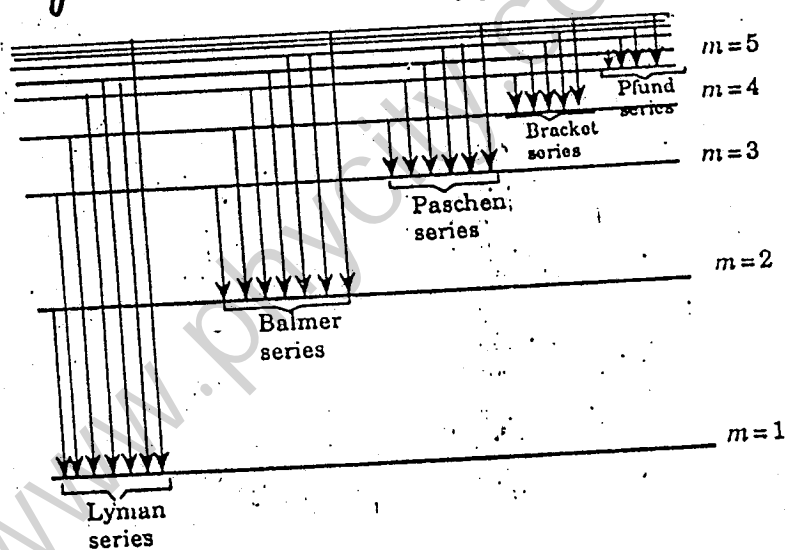
## ENERGY LEVELS OF ELECTRONS

We have found that the energy of the electron in any  $n^{\text{th}}$  orbit is given by,

$$E_n = -\frac{m_e Z^2 e^4}{8 \epsilon_0^2 h^2} \cdot \frac{1}{n^2}$$

Putting  $n=1, 2, 3, \dots$  we get energies of the electron in the I<sup>st</sup>, II<sup>nd</sup>, III<sup>rd</sup> and so on orbits. This shows that the electron has discrete values of energy. It is called quantization of energy. Each energy state is called an energy level. The series in the hydrogen atom are evolved when the electron jumps from high energy level to lower energy level.

Fig. shows the energy level diagram.

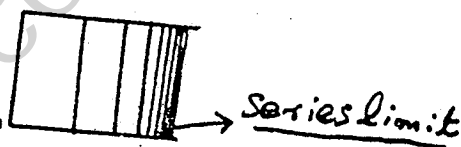


## ATOMIC SPECTRUM (SPECTRUM OF HYDROGEN)

It is observed that the elements can be made to emit light under certain conditions e.g., this can be done by passing an electric discharge through the element in gaseous state or vapour state. When the discharge passes, the atoms of the gas are excited. When these excited atoms return to their normal states, light is emitted. This light contains different wave lengths. When a fine beam of this light is made to fall on a prism or grating, the light is

splitted up into different colours in the form of a spectrum.  
 When this spectrum is viewed through a spectrometer we get as many images of the slit of the spectrometer as the number of wave lengths present in the source of light. These images of the slit are called spectral lines. The wave length of each spectral line can be found accurately.

Hydrogen has the simplest structure so its spectrum is also simple. In the spectrum of hydrogen five series of spectral lines have been found. Out of these five series only one series lies in the visible region. This series was studied by John Balmer and is called Balmer series. Balmer observed about 40 lines in this series. It is found that the distance between the lines decreases from one end to the other till they merge into one called series limit.



The wave lengths of the spectral lines in Balmer series is found by the empirical formula.

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

where  $n$  is a number greater than 2.  
 $R$  is a constant whose value is determined by Rydberg and is called Rydberg constant.

The other series in the hydrogen spectrum were discovered by Lyman, Paschen, Brackett and Pfund and are known as Lyman series, Paschen series, Brackett series and Pfund series respectively.

- Lyman series lies in ultraviolet region.
- Balmer series lies in visible region.
- Paschen series lies in infrared region.
- Brackett series lies in infrared region.
- Pfund series lies in infrared region.



$$\frac{1}{\lambda} = R \left( \frac{1}{m^2} - \frac{1}{n^2} \right), \quad n > m$$

where  $m = 1, 2, 3, \dots$

$n = m+1, m+2, \dots$

For  $m=1$  we get Lyman Series.

For  $m=2$  we get Balmer Series.

For  $m=3$  we get Paschen Series.

For  $m=4$  we get Brackett Series.

For  $m=5$  we get Pfund Series.

So we find that if electron jumps from any high energy level to state  $m=1$  then Lyman series is produced and when electron jumps from any high energy level to  $m=2, 3, 4, 5$ , then we get Balmer, Paschen, Brackett and Pfund respectively. It is also clear from the energy level diagram. In the energy level diagram, the horizontal lines represent energy levels and vertical arrows represent transitions.

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# Wave Length of First Three Lines of Balmer Series

Now the wave length of spectral lines of Balmer series is given by,

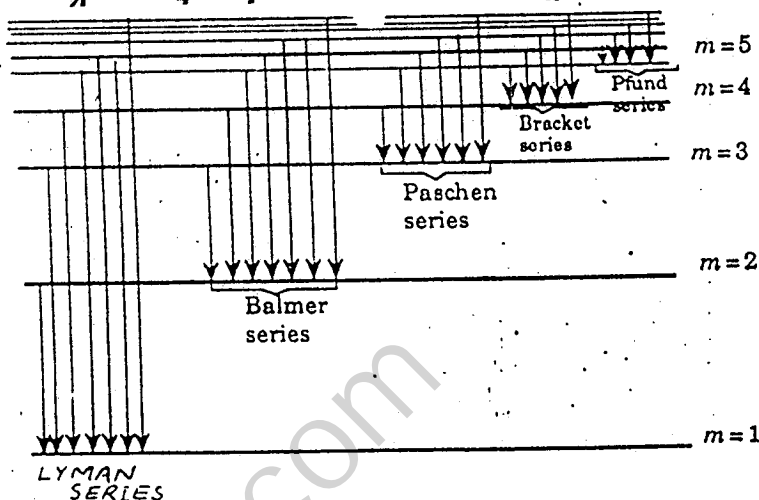
$$\frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right)$$

For first line  $n=3$

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

Now the value of  $R$  is,

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



Fig

$$\therefore \frac{1}{\lambda_1} = 1.0974 \times 10^7 \left( \frac{1}{4} - \frac{1}{9} \right)$$

$$\lambda_1 = 6561 \times 10^{-10} \text{ m}$$

$$\lambda_1 = 6561 \text{ \AA}$$

For II<sup>nd</sup> line  $n=4$

$$\therefore \frac{1}{\lambda_2} = R \left( \frac{1}{2^2} - \frac{1}{4^2} \right)$$

$$= 1.0974 \times 10^7 \left( \frac{1}{4} - \frac{1}{16} \right)$$

$$\lambda_2 = 486 \times 10^{-10} \text{ m}$$

$$\lambda_2 = 4860 \text{ \AA}$$

For III<sup>rd</sup> line  $n=5$

$$\therefore \frac{1}{\lambda_3} = R \left( \frac{1}{2^2} - \frac{1}{5^2} \right)$$

$$= 1.0974 \times 10^7 \left( \frac{1}{4} - \frac{1}{25} \right)$$

$$= 1.0974 \times 10^7 \left( \frac{25-4}{100} \right)$$

$$\lambda_3 = 4330 \text{ \AA}$$

Similarly we can calculate wave lengths of other lines in Balmer series by putting  $n=6, 7, 8, \dots$

## SPACE QUANTIZATION

The orbits of electrons can't occupy all positions in space. They occupy only certain discrete positions.

Similarly the angular momentum of an electron which is a vector quantity cannot occupy all positions in space i.e, it can have only certain discrete orientations. So angular momentum of electron can't have all directions in space. This means that not only the magnitude of angular momentum is quantized but also its direction is quantized.

"The condition which quantizes the direction of angular momentum vector is called space quantization."

So angular momentum is doubly quantized, in both magnitude and direction.

If we denote the angular momentum of electron by  $\vec{L}$ . Then two quantum numbers are needed to represent it.

One quantum number is 'l' which is called orbital quantum number. This quantum number 'l' is associated with magnitude of orbital angular momentum.

The other quantum number is 'm<sub>l</sub>' which is called magnetic quantum number. This quantum number 'm<sub>l</sub>' is associated with direction of orbital angular momentum.

The orbital quantum number l can have values,

$$l = 0, 1, 2, \dots, n-1$$

and magnetic quantum number m<sub>l</sub> can have values,

$$m_l = 0, \pm 1, \pm 2, \dots, \pm l$$

## QUANTIZATION OF MAGNITUDE OF $\vec{L}$

By Quantum mechanics the magnitude of angular momentum vector  $\vec{L}$  of electron is given by,

$$L = \sqrt{l(l+1)} \hbar$$

## QUANTIZATION OF DIRECTION OF $\vec{L}$

The space quantization demands that direction of angular momentum vector  $\vec{L}$  should also be quantized. For this purpose select any arbitrary direction e.g., Z-axis. Then we determine the direction of  $\vec{L}$  w.r.t Z-axis.

It is found that  $\vec{L}$  can't have all directions w.r.t Z-axis. But it can have only those directions which have component of  $\vec{L}$  along Z-axis. The component of  $\vec{L}$  along Z-axis is given by,

$$L_z = L \cos \theta$$

From Quantum mechanics

$$L_z = m_l \hbar$$



The possible values of  $m_l$  for a given value of  $l$  are from  $+l$  through 0 to  $-l$ . e.g., for  $l=2$ , the possible values of  $m_l$  are  $+2, +1, 0, -1, -2$ . So  $L_z$  can have the values  $0, \pm 2\hbar, \pm\hbar$ . It means only five components in all.

It means that  $L_z$  is quantized. The quantization of  $L_z$  means that angle  $\theta$  between  $\vec{L}$  and Z-axis is also quantized. The value of  $\theta$  can be found by the relation.

$$L_z = L \cos \theta$$

$$\cos \theta = \frac{L_z}{L}$$

$$\cos \theta = \frac{L_z}{\sqrt{l(l+1)} \hbar}$$

$$\therefore L_z = m_l \hbar$$

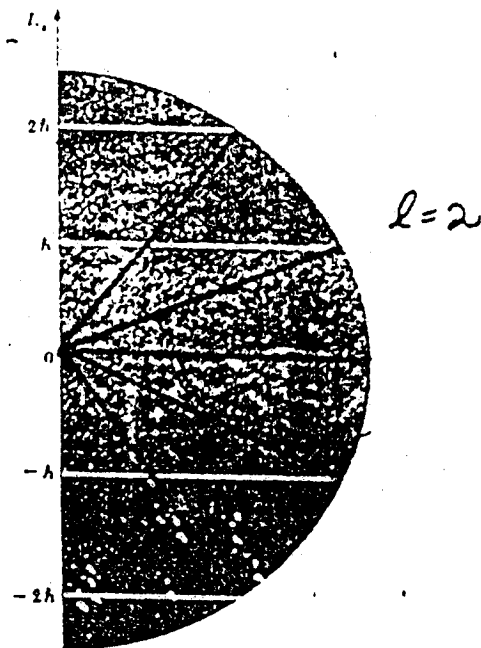
$$\therefore \cos \theta = \frac{m_l \hbar}{\sqrt{l(l+1)} \hbar}$$

$$\cos \theta = \frac{m_l}{\sqrt{l(l+1)}}$$

$$\theta = \cos^{-1} \frac{m_z}{\sqrt{l(l+1)}}$$

It shows that  $\theta$  is minimum when  $m_z$  is max. and vice versa.

The following figure shows the space quantization of the orbital angular momentum of H-atom for  $l=2$ .



## MAGNETIC MOMENT AND BOHR'S MAGNETON

Let us calculate the magnetic moment of a revolving electron. Because the revolving electron of atom behaves like electronic current flowing in a ring and so it produces a magnetic field. So the current  $I$  due to the revolution of electron in an orbit is given by  $I = \frac{e}{T}$ , where 'e' is charge of electron and 'T' is the time period.

Now the magnetic moment  $\mu$  of the current flowing in a single loop is given by,

$$\mu = \text{Area of the loop} \times \text{current}$$

$$\mu = A \times I \quad \because I = \frac{e}{T}$$

$$\therefore \mu = \frac{Ae}{T} \quad \text{--- (1)}$$

Now the areal velocity of the electron is given by,

$$\text{Areal velocity} = \frac{1}{2} r^2 \frac{d\theta}{dt}$$

$$\therefore \text{Area of the loop} = \int \frac{1}{2} r^2 \frac{d\theta}{dt} dt \quad \text{--- (2)}$$

Now the angular momentum of the electron is given by,

$$P = mvr = m r \omega r = m r^2 \omega = m r^2 \frac{d\theta}{dt}$$

$$\therefore P = m r^2 \frac{d\theta}{dt}$$

$$\frac{1}{2} |\vec{r} \times \frac{d\vec{r}}{dt}|$$

$$\frac{1}{2} |\vec{r} \times \vec{v}|$$

$$\frac{1}{2} r v$$

$$\frac{1}{2} r r \omega$$

$$\frac{1}{2} r^2 \omega$$

$$\frac{1}{2} r^2 \frac{d\theta}{dt}$$

$$\theta = 90^\circ$$

$$\omega = \frac{d\theta}{dt}$$

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$$\frac{p}{m} = r^2 \frac{d\theta}{dt}$$

$$\therefore \frac{p}{2m} = \frac{1}{2} r^2 \frac{d\theta}{dt}$$

$\therefore$  Equation (2) becomes,

$$\text{Area of loop} = \int_0^T \frac{p}{2m} dt$$

$$\therefore \text{Area of loop} = \frac{p}{2m} \int_0^T dt \quad \because \frac{p}{2m} \text{ is constant}$$

$$\therefore A = \frac{pT}{2m}$$

$$\therefore A = \frac{pT}{2m}$$

Putting the value of A in (1) we get,

$$\mu = \frac{\frac{pT}{2m} e}{T}$$

$$\mu = \frac{pT e}{2mT}$$

$$\mu = \frac{pe}{2m}$$

According to quantum theory,

$$p = l \frac{h}{2\pi}$$

where  $h$  is Planck's constant and  $l$  is orbital quantum number.

$$\therefore \mu = \frac{l \frac{h}{2\pi} e}{2m} = \frac{l h e}{4\pi m}$$

$$\therefore \mu = \frac{l h e}{4\pi m} \quad \text{--- (A)}$$

where  $l$  is the orbital quantum number which can have values  $0, 1, 2, 3, \dots, n-1$ .

where  $n$  is called principal quantum number.

From eq. (A) we see that,

$$\mu = 0 \quad \text{if } l = 0$$

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$$\mu = \frac{he}{4\pi m} \quad \text{if } l=1$$

$$\mu = \frac{2he}{4\pi m} \quad \text{if } l=2$$

$$\mu = \frac{3he}{4\pi m} \quad \text{if } l=3$$

Hence the magnetic moment of an electron due to its revolution is an integral multiple of  $\frac{he}{4\pi m}$ .

This quantity " $\frac{he}{4\pi m}$ " is the smallest quantity in terms of which the magnitudes of atomic moments are measured and is called "BOHR MAGNETON." It is denoted by  $\mu_B$ .

$$\therefore \mu_B = \frac{he}{4\pi m}$$

### VALUE OF $\mu_B$

The value of  $\mu_B$  is given by,

$$\begin{aligned} \mu_B &= \frac{he}{4\pi m} \\ &= \frac{6.625 \times 10^{-34} \times 1.6 \times 10^{-19}}{4 \times 3.14 \times 9.1 \times 10^{-31}} \\ &= \frac{6.625 \times 1.6}{4 \times 3.14 \times 9} \times 10^{-34-19+31} \\ &= \frac{10.6}{114.296} \times 10^{-22} \text{ J/T} \\ &= 0.09274 \times 10^{-22} \text{ J/T} \\ &= 9.274 \times 10^{-24} \text{ J/T} \\ &= \frac{9.274 \times 10^{-24}}{1.6 \times 10^{-19}} \text{ eV/T} \\ &= 5.79 \times 10^{-24+19} \text{ eV/T} \end{aligned}$$

$$\boxed{\mu_B = 5.79 \times 10^{-5} \text{ eV/T}}$$

### TYPICAL QUESTION

How will you determine the magnetic moment of electron and hence evaluate Bohr magneton.

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## 7. ELECTRON SPIN

The complex fine structure of the  $H_{\alpha}$  line (first line of Balmer Series in the spectrum of Hydrogen) could not be explained on the basis of Bohr's atom model even with Sommer field modifications of elliptical orbits and variation of mass of electron with velocity.

We know that the sodium light contains two wave lengths and gives two spectral lines  $D_1$  and  $D_2$  with a separation of  $6\text{ \AA}$ . When the sodium source is placed in a magnetic field of moderate strength, the  $D_1$  line splits into 4 lines while the  $D_2$  line splits into 6 lines. This splitting of a spectral line into a number of component lines in the presence of a weak magnetic field is called "Anomalous Zeeman Effect".

To explain the Zeeman effect, Uhlenbeck and Goudsmit gave a new hypothesis according to which, Each electron performs a rotation about its own axis in addition to its motion about the nucleus.

We know that when a body moves about an axis, it gives rise a mechanical angular momentum and if it is charged, it also gives rise to a magnetic moment. Thus the motion of a charged body about an axis produces a mechanical moment and a magnetic moment.

Due to the spin of electron, there are thus two motions of electron. One is orbital motion and other is spin motion. So there are two angular momenta and two magnetic moments.

Now the spin  $m_s$  is also quantized like orbital motion. So a new quantum number called spin quantum number has also been introduced.



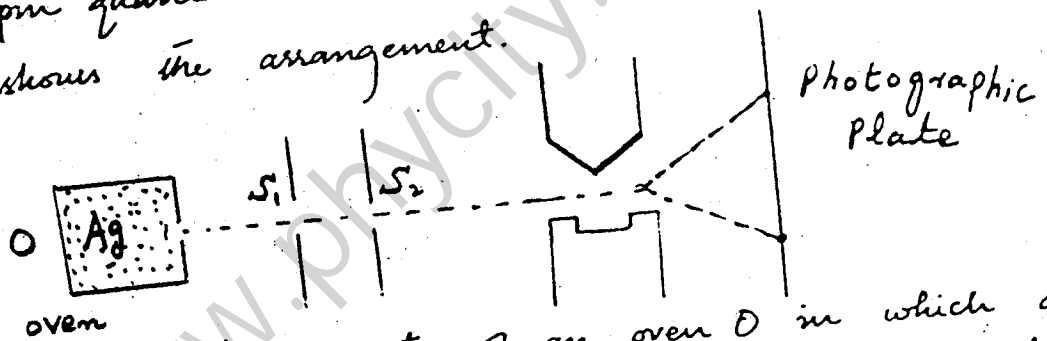
This quantum number is given the value  $\pm \frac{1}{2}$ . Where +ve sign is for anticlockwise and -ve for clockwise direction. This quantum number is denoted by  $S$ . So an electron has two types of angular momenta and two types of magnetic moments.

## 9. STERN-GERLACH EXPERIMENT

Stern and Gerlach performed an experiment to prove the existence of the magnetic moment and also to show the way in which it orientates in a magnetic field.

This experiment measures the magnetic moments of the atom and also verifies the concept of space quantization. This experiment also proves that the spin quantum number  $S$  of an atom =  $\frac{1}{2}$ .

Fig. shows the arrangement.



It consists of an oven  $O$  in which a sample of  $Ag$  was heated till it vaporized and stream of vapours from the oven  $O$  emerges out with velocities depending upon the oven temperature.

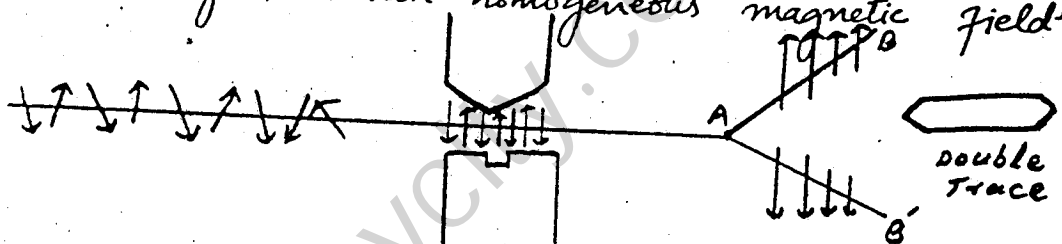
The slits  $S_1$  and  $S_2$  help further to obtain a fine pencil of atoms. This fine beam of silver atoms enters a non uniform magnetic field of an electromagnet by taking the two pole pieces one having a pointed end, the other flat with a groove on it. A very large field gradient is obtained because the magnetic lines

(1)

of force concentrate at the pointed end and so the field strength is considerably greater at the pointed end than at the other pole piece. The whole apparatus is highly evacuated so that the Ag atoms suffer no collisions in their path.

This beam of Ag atoms finally strikes a photographic plate 'P' where traces are formed.

In the absence of magnetic field, a sharp line was produced on the photographic plate. Also outside the magnetic field the magnetic moments were oriented at random as shown in the fig below. But on passing the beam through a non homogeneous magnetic field,



the magnetic moments oriented parallel and antiparallel to the direction of the magnetic field. These magnetic moments are then said to be space quantized. So in this way the concept of space quantization is verified by this experiment. Due to large magnetic field, the beam of Ag atoms was divided into two parts AB and AB as shown above. So two traces were (double trace) obtained on the photographic plate.

This experiment is in perfect agreement with the theory.

The total angular momentum of an atom is

$$J = L + S$$

where  $L$  = Orbital angular momentum.

and  $S$  = Spin angular momentum.

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For Silver  $L = 0, S = \frac{1}{2}$ .

$$\text{So } J = 0 + S$$

$$J = S = \frac{1}{2}$$

$\therefore$  Number of allowed orientations  $= 2J + 1 = 2 \times \frac{1}{2} + 1 = 2$

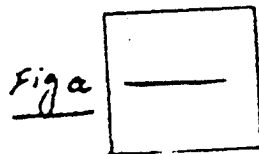
That is why two traces are obtained on the photographic plate. So with the help of this experiment it is established that value of spin quantum number  $S = \frac{1}{2}$ . Because it is the only assumption on the basis of which we get two orientations of magnetic moments (atomic magnets). Because if there were no spin of electron, there would have been no splitting up of the Ag beam into two components.

So this experiment not only proves the concept of space quantization but it also proves that the spin quantum number for the atom has  $\frac{1}{2}$  value.

## The Experimental Results

When the electromagnet of fig (a) is turned off, there is no deflection of the atoms and silver beam forms a narrow line on the screen as shown in fig. (a).

When the electromagnet is turned on, then,



(i) If there is no space quantization, then the line on the screen just expands.

(ii) If space quantization exists then the beam splits into two lines as shown in fig (b).

So this experiment clearly shows that space quantization exists.

So this experiment verifies the concept of space quantization.

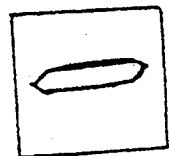


Fig b

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## 8- VECTOR ATOM MODEL

As we know that the electron can have different kinds of momenta moments which are all vectors.

The atomic model based on these vectors is called "Vector Atom Model."

In vector atom model each electron is given a quantum number.

Following are the quantum numbers assigned to the electron in vector atom model.

### i- Principal Quantum Number (n)

This quantum number is same as in Bohr's theory. This quantum determines the energy of electron in an atom and the average distance between the electron and the nucleus. It describes the motion of electron in an orbit and gives the number of shell or orbit. The energy levels K, L, M, N, O, P and Q correspond to  $n = 1, 2, 3, 4, 5, 6$  and  $7$  respectively. So  $n$  can have values  $1, 2, 3, \dots$

### - The Orbital Quantum Number (l)

This quantum number gives the shape of an orbital. It can have values  $0, 1, 2, 3, \dots (n-1)$ . It is also called secondary quantum number. The value of 'l' tells whether the orbital is spherical, dumbbell shaped or even more complicated.

In spectroscopy an electron with  $l = 0, 1, 2$  etc is said to be s, p, d electron respectively.

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### iii- The Magnetic Quantum Number ( $m_l$ )

This quantum number is associated with direction of angular momentum of orbiting electron. It can have values,

$$m_l = 0, \pm 1, \pm 2, \dots, \pm l$$

So  $m_l$  ranges from 0 to  $\pm l$ .

### iv- Spin Quantum Number (S)

This quantum number is associated with the spin of an electron in the atom. It can have values of  $+\frac{1}{2}$  and  $-\frac{1}{2}$ . The +ve and -ve signs represent the electron spinning in clockwise or anticlockwise direction. This quantum number is denoted by 'S'.

