

ATOMIC STRUCTURE - I

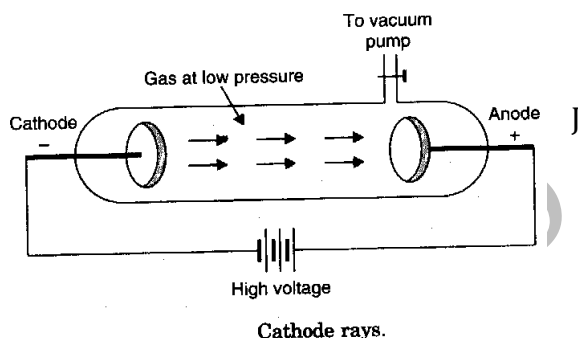
**Atom as indivisible part of matter - Dalton**

**Cathode Rays (Discovery of Electron)**

William Crooke passed high voltage electric current (10000 V) through a discharge tube, in which a gas was taken at low pressure (0.01 mm Hg). It was observed that certain rays were emitted from cathode plate which travelled in straight line at right angle to the cathode plate.

These rays are known as cathode rays.

Properties of cathode rays were studied by Sir J. Thomson:



1. **Travel in straight line** : When a metal cross (opaque substance) is placed in the path of cathode rays, its shadow is obtained. It shows that cathode rays travel in straight line.
2. **Consist of Material Particles** : When a light paddle wheel is placed in the path of cathode rays, it starts rotating. It shows that cathode rays consist of material particles.
3. **Effect of Electric/Magnetic Field** : When cathode rays are passed through electric field, they are deviated towards positive plate. It shows that cathode ray particles carry negative charge. Similarly when magnetic field is applied cathode rays are deflected in a way which also shows that cathode ray particles carry negative charge.

Sir J. J. Thomson determined **e/m** for cathode ray particles to be  $1.76 \times 10^8$  C/g. The cathode ray particles were called as **electron**.

Charge over electron was determined by **R. A. Milikan** by his **Oil drop experiment** as  $1.60 \times 10^{-19}$  C.

Since  $e/m = 1.76 \times 10^8$  C/g and  $e = 1.60 \times 10^{-19}$  C

So  $m = \frac{1.60 \times 10^{-19}}{1.76 \times 10^8} \text{ g} = 9.1 \times 10^{-28} \text{ g} = 9.1 \times 10^{-31} \text{ kg}$

4. When cathode rays strike a metal foil, it become hot.
5. Cathode rays ionize gases.
6. When cathode rays strike hard metals X-rays are produced.
7. Cathode ray effect the photographic plate. **Television picture tube is a cathode ray tube.**

**Electron** : It is a sub-atomic particle. It carries unit negative charge ( $- 1.60 \times 10^{-19}$  C) and its mass is equal to  $9.1 \times 10^{-31}$  kg. Nature of cathode ray particle is same irrespective of the nature of gas taken in the discharge tube.

**Origin of Cathode Rays** : In the beginning some electrons are emitted from the cathode. These are accelerated by high potential. These fast moving electrons knock out electrons from the atoms which come in their path thus forming a stream of electron i.e. cathode rays. *Cathode rays are emitted from cathode.*

**Justify the statement that electron is the universal or essential constituent of matter:**

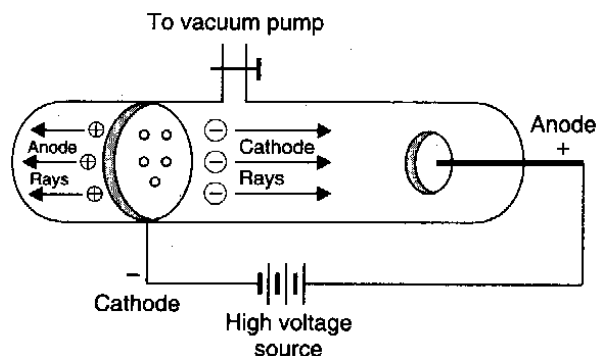
1. Any gas may be taken in the discharge tube, electrodes of any metal may be taken, discharge tube of any material may be taken but the nature of cathode ray particles i.e. electrons remain same i.e. unit negative charge ( $- 1.60 \times 10^{-19}$  C) and mass equal to  $9.1 \times 10^{-31}$  kg.
2. Some metals on heating also give electrons having same nature.

3. Some metals when exposed to sunlight also emit out electrons.
4. Radioactive elements also emit out electrons.

*It shows that electron is present in every matter  
i.e. electron is essential constituent of matter.*

### Discovery of Anode Rays (Discovery of Proton)

Goldstein applied high potential to a gas in a discharge tube at low pressure (0.01 mm Hg) using a perforated cathode. Goldstein observed as cathode rays travel towards anode and certain rays move in opposite direction, pass through perforated cathode and strike zinc sulphide coated walls of discharge tube. These rays are known as anode rays.



### Properties of Anode rays:

**Travel in straight line** : When a metal cross (opaque substance) is placed in the path of anode rays it cast its shadow showing that anode rays travel in straight line.

1. **Consist of Material Particles** : When a light paddle wheel is placed in the path of anode rays, it start rotating showing that anode rays consist of material particles.
2. **Effect of Electric/Magnetic Field** : When anode rays are passed through electric field, they are deviated towards negative plate showing that anode ray particles carry positive charge.

Nature of anode ray particles depend upon the nature of gas taken in the discharge tube. The mass of anode ray particle is equal to the mass of one atom of gas taken in the discharge tube. The anode ray particles, when hydrogen gas is taken in the discharge tube have unit positive charge and mass equal to the mass of one atom of hydrogen. These particles are known as proton.

**Proton** : It is a sub-atomic particle. It carries unit positive charge ( $+ 1.60 \times 10^{-19}$  C) and its mass is equal to the mass of one hydrogen atom ( $1.67262 \times 10^{-27}$  kg).

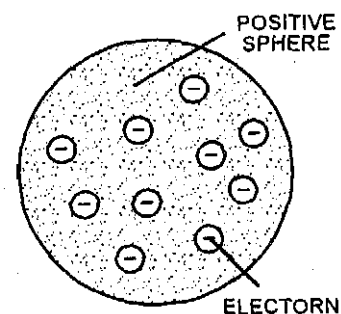
**Origin of Anode Rays** : Produced in space between anode and cathode and are produced by knocking out of electrons from the gaseous atom by high speed electrons.

**Discovery of Neutron** : Chadwick bombarded lighter element like 'Be' and 'B' by high speed  $\alpha$ -particles and discovered a neutral particle having mass equal to the mass of one atom of Hydrogen. This neutral particle is known as Neutron.

**Neutron**:- It is a sub-atomic particle. It has no charge and mass is equal to the mass of one atom of hydrogen ( $1.67493 \times 10^{-27}$  kg)

### Thomson Model of atom:-

According to J.J. Thomson Atom has a sphere of positive charge in which sufficient number of electrons are embedded. The force of repulsion between electrons is balanced by force of attraction between electrons and centre of positive charge. This model is called Raisin-Pudding model or watermelon model.



### Rutherfords scattering experiment [Discovery of nucleus]

Rutherford bombarded thin foils of metals (like Gold, Silver) with high speed  $\alpha$  - particles and observed.

**Nishant Gupta, D-122, Prashant vihar, Rohini, Delhi-85**

**Contact: 9953168795, 9268789880**

1. Most of the  $\alpha$ -particles (99.9%) pass through thin metals plates unaffected.

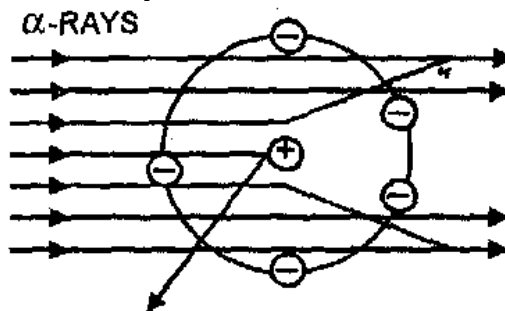
**Conclusion:-** Atom is hollow having largely empty space

2. Few of the  $\alpha$ -particles are deviated from their path.

**Conclusion:-** Atom has some positively charge part. Those  $\alpha$ - particles which come nearer to this positively charged part are deviated due to force of repulsion between similar charges. This positively charged part is known as nucleus.

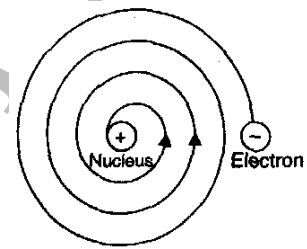
3. Very few  $\alpha$ -particles (one in 20,000) are reversed back.

**Conclusion:-** Those  $\alpha$ -particles which directly hit the nucleus are reversed back. Since the number of such particles is very small so size of the nucleus is also very small.



### **Rutherfords nuclear model of atom**

1. Atom has positively charged nucleus present at the centre occupying small space whole mass of the atom is concentrated in the nucleus.
2. Electrons revolve around the nucleus in circular path.
3. Force of attraction between nucleus and electron is balanced by centrifugal force due to circular motion of electrons.



Gradual decrease in the radius of orbit.

### **Limitations of Rutherford's model of atom**

According to Maxwell if a charged body is in acceleration, it loses energy gradually. As electron is a charged particle and as it is moving in a circular path so it is also in acceleration so electron should lose energy gradually and should collapse in the nucleus acquiring a spiral path. Actually it does not happen.

**Atomic Number:-** Number of protons present in the nucleus of an atom.

**Nucleons:-** Particles present in the nucleus i.e protons and neutrons

**Mass Number** = No. of protons + No. of neutrons

$A \rightarrow$  Mass No.

${}_z X \rightarrow$  symbol .

$\downarrow$

Atomic No.

In neutral atom No. of electrons = No. of protons = Atomic No.

In Cation No. of electrons = Atomic No.- Charge

In Anion No. of electrons = Atomic No.+ Charge

### **Exercise 1:**

1. Calculate the number of protons, neutrons find electrons in  ${}_{35}^{80}\text{Br}$  .

2. Find out the atomic number, mass number, number of protons, electrons and neutrons present in the element with the notation  ${}_{92}^{238}\text{U}$

- The nuclear radius is of the order of  $10^{-13}$  cm while atomic radius is of the order  $10^{-8}$  cm. Assuming the nucleus and the atom to be spherical, what fraction of the atomic volume is occupied by the nucleus ?
- The number of electrons, protons and neutrons in a species are equal to 18, 16 and 16 respectively. Assign the proper symbol to the species.

Particle	Mass No.	Atomic No.	Protons	Neutrons	Electrons
Nitrogen atom	—	—	—	7	7
Calcium ion	—	20	—	20	—
Oxygen atom	16	8	—	—	—
Bromide ion	—	—	—	45	36

- Calculate the percentage of higher isotope of neon which has atomic mass 20.2 and the isotopes have the mass numbers 20 and 22.

**Isotopes :-** Atom of same element (same atomic no.) with different mass number are known as isotope



**Isobars :-** Atom of different elements (different atomic number) with same mass number are called as isobars  ${}^{40}_{18}\text{Ar}, {}^{40}_{19}\text{K}, {}^{40}_{20}\text{Ca}$

**Isotones :-** Atoms of different elements having same number of neutrons  ${}^{14}_6\text{C}, {}^{15}_7\text{N}, {}^{16}_8\text{O}$

### **Isoelectronic**

The specie (Atoms or Ions) having same number of electrons.

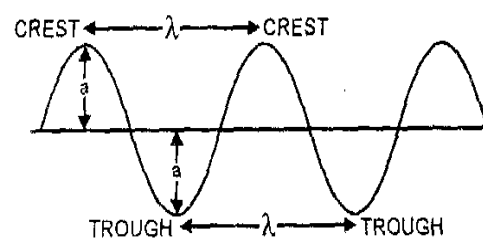


Radii of an atom are of the order of  $10^{-10}$  m and that of nucleus =  $10^{-15}$  m

$$V = R_0 \times A^{1/3} \quad R_0 = 1.4 \times 10^{-15} \text{ m}; A = \text{Mass number}$$

### **Electromagnetic Wave Theory:-** [James Clark Maxwell]

- Energy is emitted from any source continuously in the form of radiations (wave) and is known as radiant energy.
- Radiant energy propagates in the form of wave which are associated with both electric and magnetic field so these waves are known as electromagnetic waves and radiations as electromagnetic radiations.
- These waves do not require any material medium for propagation.



### **Some characteristics of a wave**

**Wave Length ( $\lambda$ ):-** Distance between any two consecutive crests or troughs on a wave expressed in  $\text{A}^0$  ( $1\text{A}^0 = 10^{-10}\text{m}$ );  $\text{nm} = (1\text{nm} = 10^{-9}\text{m})$ ;  $\text{pm} = (1\text{pm} = 10^{-12}\text{m})$

**Frequency ( $\nu$ ):-** Number of waves passing through a point on a wave in one second. Expressed in Hertz (Hz) =  $1 \text{ Hz} = 1 \text{ Cycle s}^{-1}$

**Velocity of a wave (c)** Linear distance travelled by a wave in one second  $c = 3 \times 10^8 \text{ ms}^{-1}$

**Amplitude of a wave (a):-** Height of a crest or depth of trough.

**Wave Number ( $\bar{\nu}$ )** = No. of waves present in unit length ie Reciprocal of wave length.  $\bar{\nu} = \frac{1}{\lambda}$

**Time Period** = Reciprocal of frequency

Period =  $1/\nu$ ;

$c = \nu \times \lambda$

or  $\nu = c/\lambda$  or  $\lambda = c/\nu$

Order of wavelengths of different electromagnetic radiations

Radio wave > Microwave > Infrared > Visible Ultra-violet > X-rays >  $\gamma$  rays > cosmic rays

### Exercise 2:

1. Calculate (a) wave number (b) frequency of yellow radiation having wavelength of 5800 Å
2. A particular radio station broad- casts .At a frequency of 1120 kHz (kilohertz). Another radio station broadcasts at a frequency of 98.7 MHz (Megahertz). What are the wavelengths of the radiations from each station?
3. Calculate the Frequency of infrared radiations having wavelength,  $3 \times 10^6$  nm. [Ans.  $10^{11} \text{ s}^{-1}$ ]
4. Calculate the wave number of radiations having a frequency of  $4 \times 10^{14}$  Hz. [Ans.  $1.33 \times 10^4 \text{ cm}^{-1}$ ]
5. The Vividh Bharati station of All India Radio, Delhi broadcasts at a frequency of 1368 kHz (kilohertz). Calculate the wavelength of the electromagnetic radiation emitted by the transmitter. Which part of the electromagnetic spectrum does it belong to?  
[Ans. 219.3 m, Radiowave]
6. The wavelength range of the visible spectrum extends from violet (400 nm) to red (750 nm). Express these wavelengths in frequencies (Hz) ( $1 \text{ nm} = 10^{-9} \text{ m}$ )  
[Ans.  $4.0 \times 10^{14}$  to  $7.5 \times 10^{14}$  Hz]
7. Calculate (a) wave number (b) frequency of yellow radiation having wavelength of 5800 Å  
[Ans. (a)  $1.724 \times 10^4 \text{ cm}^{-1}$  (b)  $5.172 \times 10^{14} \text{ s}^{-1}$ ]

### Plank's Quantum Theory

1. Radiant energy can neither be emitted nor absorbed continuously. If energy is emitted or adsorbed it is done discontinuously in the form of some packets.
2. Each packet of energy is known as quantum. In case of light energy is known as photon.
3. Energy of each photon (quantum) is directly proportional to its frequency.

$$E \propto \nu \quad E = \text{quantum of energy}$$

$$E = h\nu \quad h = \text{Plank's Constant} = 6.626 \times 10^{-34} \text{ JS}$$

$$\therefore \nu = \frac{c}{\lambda} \quad \nu = \text{frequency}$$

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

### Exercise 3:

1. Calculate the frequency and energy of a photon of radiation having wavelength  $6000\text{\AA}$ .
2. A 100 watt bulb emits monochromatic light of wavelength 400 nm. Calculate the number of photons emitted per second by the bulb.
3. Calculate the energy of a mole of photons of radiations whose frequency is  $5 \times 10^{14} \text{ Hz}$  ?  
[Ans.  $199.51 \text{ kJmol}^{-1}$ ]
4. Which has a higher energy: a photon of red light with a wavelength of  $7500 \text{\AA}$  or a photon of green light with a wavelength of  $5250 \text{\AA}$ ?  
[Ans. Green]
5. In the infrared region of the atomic spectrum of hydrogen, a line is obtained at  $3802 \text{ cm}^{-1}$ . Calculate the energy of this photon ( $h = 7.56 \times 10^{-34} \text{ Jsec}$ )  
[Ans.  $7.56 \times 10^{-20} \text{ J}$ ]

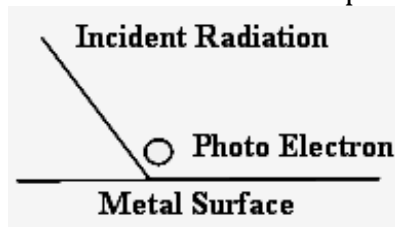
### Limitations of Electromagnetic wave theory

#### 1. Black body radiation:-

A black body is a perfect heat absorber and perfect heat emitter. When black body is heated it absorbs energy in the form of heat, but it emits out energy in the form of light. It is observed that in case of black body radiation colour of light changes from red to yellow to white. As per electromagnetic wave theory energy of radiant energy is proportional to intensity not frequency. So this theory can not explain change in colour of light emitted.

#### 2. Photoelectric effect:-

When a radiation of certain minimum frequency is incident on the surface of a metal resulting in ejection of electrons from the surface of metal. This phenomenon is known as photoelectric effect and electrons emitted are known as photoelectrons.



### Main observations in case of photoelectric effect

1. For the emission of electrons from the surface of a metal radiation of certain minimum frequency are required. This frequency is known as critical frequency or Threshold frequency ( $\nu^0$ )
2. If frequency of incident radiation is less than critical frequency. Electrons can not be emitted by increasing intensity to any extent.
3. Value of critical frequency is different in case of different metals
4. If frequency of incident radiation  $>$  Critical frequency.  
K.E. of Photoelectron  $\propto$  Frequency of incident radiation
5. If frequency of incident radiation is more than or equal to critical frequency  
No. of electrons ejected  $\propto$  Intensity of radiation

Electromagnetic wave theory fails to explain it because as per this theory energy of radiation depends upon intensity so by taking radiation of any frequency and by increasing intensity could have ejected electrons but this is not the observation.

### Einstein's explanation of Photoelectric effect

Einstein suggested by taking the basis of Plank Quantum Theory that light has particle nature.

1. One photon hits one electron on the surface of metal and transfers its energy to the electron. If frequency of incident radiation is less than critical frequency then energy acquired by the electron will not be sufficient to overcome force of attraction between

electron and surface of metal so electron will not be ejected out (Extra energy will be emitted out by electron).

2. If frequency of photon is more than critical frequency then part of energy is used to take out electron from the surface of metal and rest will change into Kinetic energy of electron

$$h\nu = h\nu^0 + \text{K.E.}$$

$$\text{K.E.} = h\nu - h\nu^0 = h(\nu - \nu^0)$$

$h\nu^0$  = Minimum energy required to remove electron from the surface of metal it is known as work function.

**Stopping Potential:-** Potential applied to photoelectron to bring it to rest.

Stopping Potential = K.E.

**Exercise 4:**

1. Calculate the kinetic energy of the electron ejected when yellow light of frequency  $5.2 \times 10^{14} \text{sec}^{-1}$  falls on the surface of potassium metal. Threshold frequency of potassium is  $5 \times 10^{14} \text{sec}^{-1}$ .
2. When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium, electrons are emitted with a kinetic energy of  $1.68 \times 10^5 \text{ J mol}^{-1}$ . What is the minimum energy needed to remove an electron from sodium? What is the maximum wavelength that will cause a photoelectron to be emitted?
3. Light of wavelength  $4000 \text{ \AA}$  falls on the surface of cesium. Calculate the energy of the photo-electron emitted. The critical wavelength or photoelectric effect in cesium is  $6600 \text{ \AA}$ .  
[Ans.  $1.95 \times 10^{-19} \text{ J}$ ]
4. The threshold energy for photo-electric emission of electrons from a metal is  $3.056 \times 10^{-15} \text{ joules}$ . If light of  $4000 \text{ \AA}$  wave length is used, will the electrons be ejected or not?  
( $h = 6.63 \times 10^{-34} \text{ Joule sec}$ ). [Ans. No]
5. The threshold frequency  $\nu_0$  for a metal is  $7.0 \times 10^{14} \text{ s}^{-1}$ . Calculate the kinetic energy of an electron emitted when radiation of frequency  $\nu = 1.0 \times 10^{15} \text{ s}^{-1}$  hits this metal.  
[Ans.  $1.988 \times 10^{-19} \text{ J}$ ]

**Electromagnetic Spectrum**

Component radiation of a light arranged in order of increasing wave length or decreasing frequencies

**Continuous Spectrum**

In the spectrum the component radiations are so continuous that each of them merges into the next

**Line Spectrum:-** When lines corresponding to different wave lengths are observed in the spectrum. It is characteristic of atoms.

**Band Spectrum:-** When bands of colours are obtained in the spectrum. Band Spectrum is characteristic of molecules.

**Emission Spectrum**

Spectrum of emitted light (when electron jump from higher shell to lower shell)

**Absorption Spectrum:-**

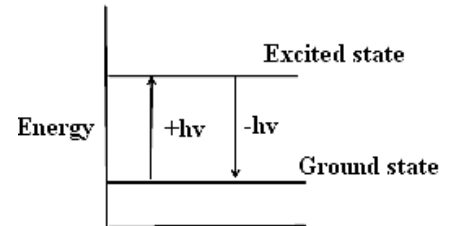
Spectrum of Absorbed light (When electron jumps from lower to higher shell)

### Line Spectrum of Hydrogen

When an electric discharge is passed through hydrogen gas at a low pressure and light so emitted is analyzed then series of spectral lines are obtained in different regions of light. This spectrum is known as line spectrum of hydrogen or atomic spectrum of hydrogen.

**Different series of lines are**

1. Lyman series in ultraviolet region of light
2. Balmer series in visible region of light
3. Paschen series in Infra red region of light
4. Brackett series in Infra red region of light
5. pfund series in Infra red region of light



### Origin of a spectral line

Electron in the ground state absorbs a quantum of energy and jumps to higher energy state i.e. excited state. The excited state is unstable and electron jumps back to ground state by giving out same quantum of energy in the form of radiation. It gives a line in the spectrum

### Explanation why large number of spectral lines are obtained in the atomic spectrum of hydrogen although it contains only one electron.

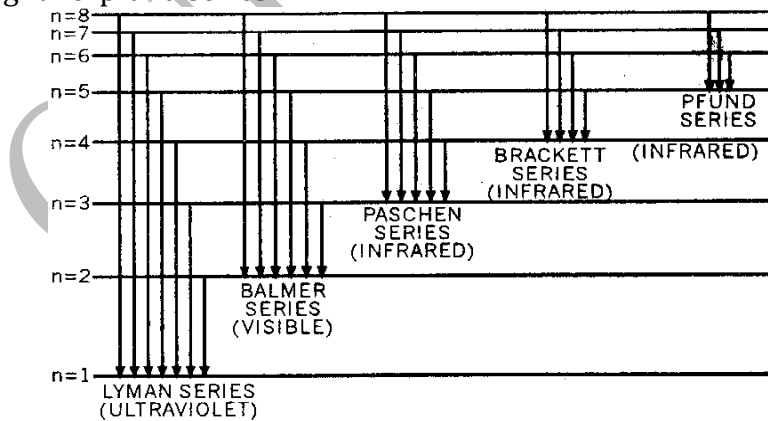
In the hydrogen atom the electron is present in the first shell in the ground state. The electron may absorb a quantum of energy and jump to higher shell (excited state). Electron may jump to 2<sup>nd</sup>, 3<sup>rd</sup>, 4<sup>th</sup>..... n<sup>th</sup> depending upon the quantum of energy absorbed.

In the discharge tube there are large numbers of hydrogen atoms. In excited state in some atoms the electron is in second shell, in some atom in third shell in some atoms in 4<sup>th</sup> shell.....n<sup>th</sup> shell.

Excited state is unstable and electron jumps back to ground state directly or in steps. If electron jumps back to 1<sup>st</sup> shell from any shell (2-1, 3-1..... $\alpha$ -1) spectral lines are obtained in ultraviolet region of light i.e Lyman series If electron jumps back to 2<sup>nd</sup> Shell form any shell spectral lines are obtained in visible region of light i.e. Balmer series.

If electron jumps back to 3<sup>rd</sup> shell from any shell spectral lines are obtained in infra red region of light i.e. Paschen series. If electron jumps back to 4<sup>th</sup> shell from any shell spectral lines are obtained in infra red region of light i.e Brackett series.

If electron jumps back to fifth shell from any shell spectral lines are obtained in infra red region of light i.e. pfund series.



Electronic transitions producing different series in the hydrogen spectrum.

$$\text{Total no. of spectral lines} = n(n-1)/2$$

n= no. of shell in which electron is present in excited state



Limiting line in a series when  $n_2 = \infty$  (This is also shortest wave length in a series)  
 Line of longest wavelength when  $n_2 =$  next higher shell.  
 Similar spectrum is shown by atoms / ions having same number of electrons.

### Rydberg Formula

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

$\bar{\nu}$  = Wave number of spectral line

$\lambda$  = wave length of spectral line

R=Ryd-berg constant ( $1.09677 \times 10^5 \text{ cm}^{-1}$  or  $1.09677 \times 10^7 \text{ m}^{-1}$ )

$n_1$  = lower shell

$n_2$  = higher shell

Z = atomic number

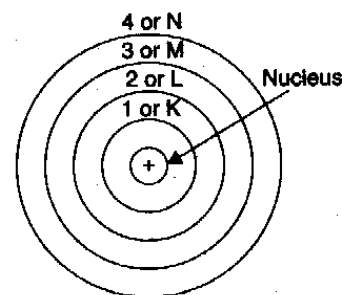
### Exercise 5:

1. Calculate the frequency and the wavelength of the radiation in nanometres emitted when an electron in the hydrogen atom jumps from third orbit to the ground state. In which region of the electromagnetic spectrum will this line lie? (Rydberg constant =  $109,677 \text{ cm}^{-1}$ )
2. The wavelength, of the first line in the Balmer series is 656 nm. Calculate the wavelength of the second line and the limiting line in Balmer series.
3. Calculate the wavelength of the spectral line obtained in the spectrum of  $\text{Li}^{2+}$  ion when the transition takes place between two levels whose sum is 4 and the difference is 2.
4. What is the frequency and wavelength of a photon emitted during a transition from  $n = 5$  state to  $n = 2$  state in the hydrogen atom?  
 [Ans. 434 nm]
5. Calculate the wavelength from the Balmer formula when  $n = 3$ . [Ans. 656 nm]
6. Calculate the wavelength of the spectral line in Lyman series corresponding to  $n_2 = 3$ .  
 [Ans. 102.6 nm]

### Bohr's Atomic Theory

Bohr's model of atom is based upon Plank Quantum Theory. Main postulates of the Theory are :

1. Atom has a positively charged nucleus presents at the centre, occupying small space. Whole mass of the atom is concentrated in the nucleus.
2. Electrons revolve around the nucleus in fixed circular paths known as shells or orbits.
3. Each shell or orbit is associated with definite amount of energy so they are also known as stationary energy levels. The shells or orbits are numbered K, L, M, N... or 1, 2, 3, 4 .... Starting from the shell nearest to nucleus.
4. When the electron is in the lowest shell or ground state the electron goes on revolving with out losing or gaining energy. The electron may absorb a quantum of energy and may jump to higher shell. This higher energy state is known as excited state. Excited state is unstable and electron jumps back to ground state by giving out same quantum of energy in the form of radiation



Bohr's orbits.

$E_2$  = Energy of higher shell;

$E_1$  = Energy of lower shell

$h$  = Plank's constant;

$\nu$  = Frequency of radiation emitted

$\lambda$  = wave length of radiation emitted;

$a$  = velocity of radiation.

5. Angular momentum of an electron in an atom can have certain definite or discrete values (Angular momentum)  $mvr = nh/2\pi$

$M$  = Mass of electron;

$v$  = velocity of electron

$r$  = radius of shell;

$n$  = number of shell

$h$  = Planks constant

6. Energy of electron in a shell in hydrogen like particle is given by

$$E_n = -\frac{2\pi^2 u e^4 z^2}{n^2 h^2}$$

$u e$  = Reduced mass of electron

$e$  = charge over the electron

$z$  = atomic number

$$\begin{aligned} E_n &= -[2.18 \times 10^{-18}] \times \frac{z^2}{n^2} \text{ J atom}^{-1} \\ E_n &= [1.312 \times 10^6] \times \frac{z^2}{n^2} \text{ J atom}^{-1} \\ E_n &= [13.6] \times \frac{z^2}{n^2} \text{ eV atom}^{-1} \end{aligned}$$

7. The radii of stationary states are

$$r_n = \frac{r_0 n^2}{z} \quad \text{Where } r_0 \text{ is radius of 1}^{\text{st}} \text{ shell of H-atom } r_0 = 0.529 \text{ \AA}$$

8. Velocity of electron in nth shell of hydrogen like particle  $v_n = v_0 \times \frac{z}{n}$   
 $v_0$  = velocity of electron in 1<sup>st</sup> shell of hydrogenation =  $2.188 \times 10^6 \text{ m s}^{-1}$

**Q.** Why energy of electron is assigned a negative value?

**Ans.** When an electron is taken at infinite distance from the nucleus so that there is no force of attraction between nucleus and electron. At this state the energy of electron is assigned a zero value as an arbitrary standard. When an electron comes nearer to nucleus there will be force of attraction between nucleus and electron. In this process energy is given out. So the energy of an electron in an atom is assigned a negative value.

### Quantization of Electronic Energy

According to Bohr's atomic theory electrons revolve in a shell without losing or gaining energy i.e. energy of electron can not change continuously but can have only definite values. So energy of an electron is quantized.

### Limitations of Bohr's atomic Theory

1. According to this theory atom is planar but actually atom is 3-dimensional.
2. It can explain the spectra of uni-electron atom/ions but fails to explain the spectra of multi-electron atoms/ions
3. When a spectrum is obtained under the influence of electric or magnetic field. Each spectral line splits into finer lines. Splitting of a line in electric field is known as **Stark effect** and in magnetic field is known as **Zeeman effect**. Bohr's theory fails to explain stark effect and Zeeman effect

### **Exercise 6:**

1. Calculate the wavelength of the radiation emitted when .in electron in a hydrogen atom undergoes a transition from 4th energy level to the 2<sup>nd</sup> energy level. In which p.irt of the electromagnetic spectrum does this line lie? [ans. 486.3 nm]
2. Calculate the energy associated with the first orbit of He<sup>+</sup> .What is the radius of this orbit?
3. Calculate the velocity of electron in the first Bohr orbit of hydrogen atom. Given that Bohr radius = 0.529 \AA

4. Calculate
- First excitation energy of the electron in the hydrogen atom.
  - Ionization energy of the hydrogen atom.
5. The ionisation energy of  $\text{He}^{2+}$  is  $8.72 \times 10^{-18} \text{ J atom}^{-1}$ . Calculate the energy of the first stationary state of  $\text{Li}^{2+}$
6. If the energy difference between two electronic states is  $214.68 \text{ kJ mol}^{-1}$ , calculate the frequency of light emitted when an electron drops from the higher to the lower state. Ans.  $5.395 \times 10^{14} \text{ sec}^{-1}$
7. Calculate the wave number for the longest wavelength transition in the Balmer series of atomic hydrogen. [Ans.  $1.523 \times 10^6 \text{ m}^{-1}$ ]

### Dual nature of matter – de Broglie Equation

According to de-Broglie all moving material particles have dual nature i.e. particle as well as wave nature. Wave associated with a material particle is known as matter wave de-Broglie derived an equation for photon assuming dual nature for it and applied it to moving material particle

If it has wave nature.

According to Plank's Quantum theory

$$E = hv = \frac{hxc}{\lambda} \dots\dots\dots(I)$$

If it has particle nature. According to Einstein

$$E = mc^2 \dots\dots\dots (II)$$

From equations I and II

$$mc^2 = h \times \frac{c}{\lambda} \text{ or } mc = \frac{h}{\lambda} \text{ or } \lambda = \frac{h}{mc}$$

If a moving particle has mass 'm' and moving with a velocity v

$$\text{Then } \lambda = \frac{h}{mv} = \frac{h}{p} \quad P = mv \text{ momentum}$$

If kinetic energy is given

$$\text{K.E.} = \frac{1}{2} mv^2$$

$$\therefore v = \sqrt{\frac{2KE}{m}}$$

If mass of particle is not given and K.E. is given then

$$v = \frac{2KE}{h}$$

Difference between Electromagnetic wave and matter wave

<b>ELECTROMAGNETIC WAVES</b>	<b>MATTER WAVES</b>
1. The electromagnetic waves are associated with electric and magnetic Fields, perpendicular to each other and to the direction of propagation.	1. Matter waves are not associated with electric and magnetic fields.
2. They do not require any medium for propagation, ie., they can pass through vacuum.	2. They require medium for their propagation, ie., they cannot pass through vacuum.
3. They travel with the same speed as that of light.	3. They travel with lower speeds. Moreover, it is not constant for all matter waves.
	4. They do not leave the moving particle,

4. They leave the source , i.e., they are emitted by the source.

5. Their wavelength is given by  $\lambda = \frac{c}{\nu}$

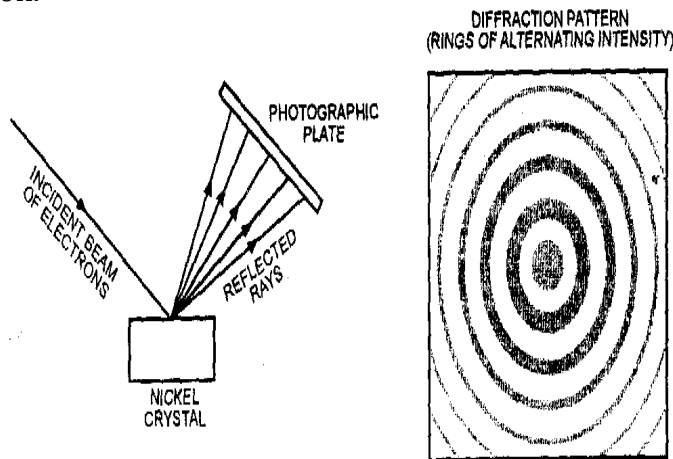
i.e., they are not emitted by the particle.

5. Their wavelength is given by  $\lambda = \frac{h}{mv}$

## Experimental verification of wave character of electron

### 1. Davisson and Germer's experiment

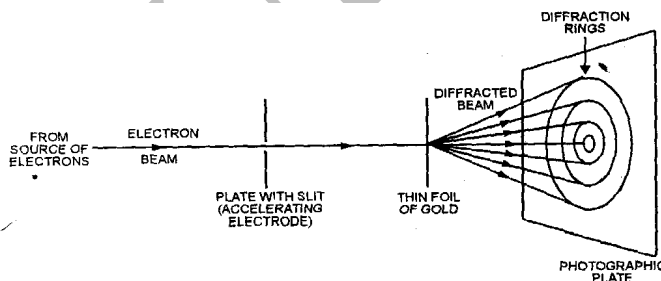
Davisson and Germer observed that when a beam of electrons is allowed to fall on the surface of a nickel crystal and the scattered or the reflected rays are received on a photographic plate a diffraction pattern (consisting of a number of concentric rings) ,similar \_to that produced—by X-rays ,is obtained . Now since X-rays are electro magnetic waves, i.e., they are confirmed to have wave character, therefore, electrons must also have wave character. Moreover, the wavelength determined from the diffraction pattern is found to be the very nearly the same as calculated from de-Broglie-equation. This further lent support to de Broglie equation.



. Diffraction of electron beam by nickel crystal (Davisson and Germer's experiment)

### 2. Thomson's experiment

Thomson's experiment. G.P. Thomson, in 1928 performed experiments with thin foil of gold in on place of nickel crystal. He observed that if the beam of electrons after passing through the thin foil of gold is received a on photographic plate placed perpendicular to the direction of the beam a diffraction pattern is observed as before .This again confirmed the wave nature of electrons.



Diffraction of electron beam by thin foil of gold ( G.P.Thomson experiment)

### **Calculation of de-Broglie wave length of electron in terms of potential applied to accelerate it**

If accelerating potential  $V$  is applied to an electron beam, the energy acquired by the electron is expressed in electron-volt (eV) which is equal to charge on the electron in

coulombs X potential applied in volts. This energy becomes the kinetic energy of the electron.

As kinetic energy =  $\frac{1}{2} mv^2$ ,

$$\text{hence, } \frac{1}{2} mv^2 = eV$$

$$\text{Or } v = \sqrt{\frac{2eV}{m}}$$

$$\text{So, } \lambda = \frac{h}{mv} = \frac{h}{m}$$

$$\frac{h}{m} \times \sqrt{\frac{m}{2eV}} = \frac{h}{\sqrt{2meV}}$$

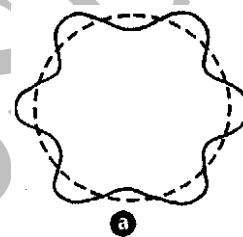
Substituting the values of various constants,  $h = 6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$

$m = 9.11 \times 10^{-31} \text{ kg}$ ,  $e = 1.602 \times 10^{-19} \text{ C}$ , we get

$$\lambda = \frac{1.226 \times 10^{-9}}{\sqrt{V}} \text{ m}$$

Thus, knowing the potential applied, the wavelength of the electron can be calculated.

These wavelengths are found to be of the same order as bond lengths of molecules. Hence, electron diffraction is used in the study of molecular structure.



### Derivation of Bohr's postulate of angular momentum from de-Broglie equation

According to Bohr's model, the electron revolves around the nucleus in circular orbits.

According to de Broglie concept, the electron is not only a particle but has a wave character.

Thus, in order that the wave may be completely in phase, the circumference of the orbit must be equal to an integral multiple of wavelength ( $\lambda$ ), i.e.,  $2\pi r = n \lambda$  ... (i) where  $r$  is the radius of the orbit and  $n$  is an integer.

But  $\lambda = h/mv$  (de Broglie equation) ... (ii)

Substituting this value of  $\lambda$  in eqn. (i), we get

$$2\pi r = n \frac{h}{mv} \quad \text{or} \quad mvr = nh/2\pi. \quad \text{Which is Bohr's postulate of angular momentum.}$$

### Exercise 7:

1. Calculate the wavelength associated with an electron (mass =  $9.1 \times 10^{-31} \text{ kg}$ ) moving with a velocity of  $10^3 \text{ m sec}^{-1}$  ( $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$ ).
2. A moving electron has  $4.55 \times 10^{-23} \text{ joules}$  of kinetic energy. Calculate its wavelength (mass =  $9.1 \times 10^{-31} \text{ kg}$ ) and ( $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$ ).
3. Calculate the mass of a photon with wavelength  $3.6 \text{ \AA}$
4. The particles A and B are in motion. If the wavelength associated with particle A is  $5 \times 10^{-8} \text{ m}$ , calculate the wavelength associated with particle B if its momentum is half of A.
5. The kinetic energy of a sub-atomic particle is  $5.85 \times 10^{-25} \text{ J}$ . Calculate the frequency of the particle wave. (Planck's constant,  $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$ )

6. Calculate the momentum of a particle which has a de Broglie wavelength of  $1 \text{ \AA}$  or  $0.1 \text{ nm}$ . ( $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$ ). [Ans.  $6.6 \times 10^{-24} \text{ kgm s}^{-1}$ ]
7. The kinetic energy of an electron is  $5 \times 10^{-5} \text{ eV}$  (electron volts). Calculate the wavelength of the wave associated with the electron. The mass of the electron may be taken as  $10^{-30} \text{ kg}$ . [Ans.  $1.65 \times 10^{-7} \text{ m}$ ]
8. A proton is moving with kinetic energy  $5 \times 10^{-27} \text{ J}$ . What is the wavelength of the de Broglie wave associated with it? [Ans.  $1.62 \times 10^{-7} \text{ m}$ ]
9. What must be the velocity of a beam of electrons if they are to display a de Broglie wavelength of  $100 \text{ \AA}$  (mass =  $9.1 \times 10^{-31} \text{ kg}$ ) ( $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$ ). [Ans.  $18.8 \text{ pm}$ ]
10. A tennis ball of mass  $6.0 \times 10^{-2} \text{ kg}$  is moving with a speed of  $62 \text{ m s}^{-1}$ . Calculate the wavelength associated with this moving tennis ball. Will the movement of this ball exhibit a wave character? Explain. [Ans.  $1.8 \times 10^{-34} \text{ m}$  No because the wavelength is too small to be observed]
11. Calculate de Broglie wavelength of an electron moving with 1% of the speed of light. [Ans.  $2.4 \times 10^{-10} \text{ m} = 2.4 \text{ \AA}$ ]
12. Calculate the wavelength of an electron that has been accelerated in a particle accelerator through a potential difference of 100 million volts  
[  $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$ ;  $m_e = 9.1 \times 10^{-31} \text{ kg}$ ;  $h = 6.6 \times 10^{-34} \text{ Js}$ ;  $c = 3.0 \times 10^8 \text{ m/s}$  ]  
[Ans.  $12.2 \times 10^{-14} \text{ m}$ ]
13. The mass of an electron is  $9.1 \times 10^{-31} \text{ kg}$ . If its K.E. is  $3.0 \times 10^{-25} \text{ J}$ , calculate its wavelength. [Ans.  $896.7 \text{ nm}$ ]