

CHAPTER- ATOMIC STRUCTURE
(FYUGP 1st sem minor; PANDU COLLEGE)
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- Dalton, a British school teacher, in 1808, proposed that matter was made up of extremely small, indivisible particles called atoms (Greek, '*a-tomio*' meaning '*uncuttable*'). The concept continued to hold grounds for a number of years.
- However, researches done by various eminent scientists like J.J. Thomson, Goldstein, Rutherford, Chadwick, Bohr and others in the latter half of the 19th century and in the beginning of the 20th century have established, that atom was made up of smaller particles. At present, about 35 different subatomic particles are known but the three particles namely **electron**, **proton** and **neutron** are regarded as the fundamental particles.

DISCOVERY OF FUNDAMENTAL PARTICLES

Discovery of electrons: study of cathode rays

The electrical nature of matter had been indicated in very early experiments on the production of frictional electricity (i.e. rubbing of glass or ebonite rods with silk or fur). This was further confirmed by the experiments on the electrolysis of substances.

- William Crookes, in 1879, studied the conduction of electricity through gases at low pressure. For this purpose, he took a discharge tube which is a long glass tube, about 60 cm long & sealed at both the ends and fitted with two metal electrodes.

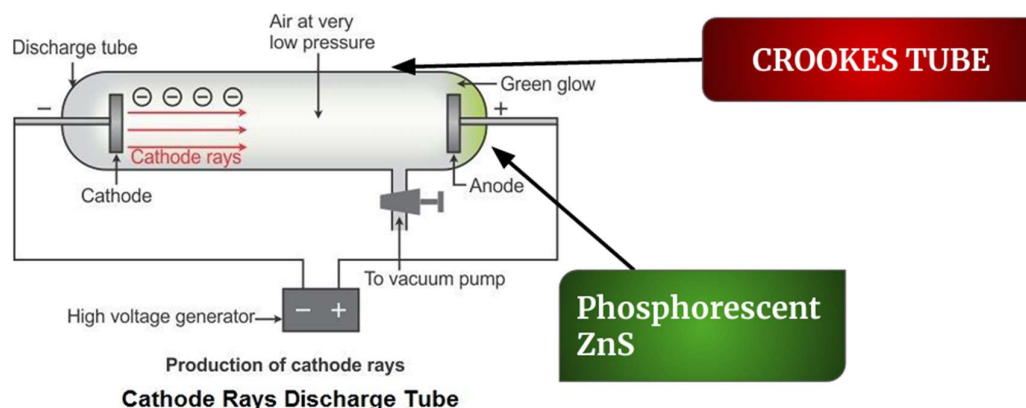


Figure 1. Experimental set-up of cathode ray discharge tube.

- It has a side tube fitted with a stop-cock (Figure 1). This tube is connected to a vacuum pump and the pressure inside the discharge tube is reduced to as low as 0.01 mm. Now

when a high voltage (nearly 10,000 volts) is applied between the electrodes, it is found that some invisible rays are emitted from the cathode. The presence of these rays is detected from the fact that the glass wall of the discharge tube opposite to the cathode begins to glow with a faint greenish light.

- **PROPERTIES OF CATHODE RAYS**

From the various experiments carried out by J.J. Thomson (1897) and others, the cathode rays have been found to possess the following properties:

- (i) They produce a sharp shadow of the solid object placed in their path. This shows that cathode rays travel in straight lines.
- (ii) If a light paddle wheel (made up of mica) mounted on an axle is placed in their path, the wheel begins to rotate. This shows that cathode rays are made up of material particles.
- (iii) When an electric field is applied on the cathode rays, they are deflected towards the positive plate of the electric Field. This shows that cathode rays carry negative charge.
- (iv) Similarly, when a magnetic field is applied on the cathode rays, these rays are deflected in a direction which shows that they carry negative charge.
- (v) When cathode rays strike a metal foil, the latter becomes hot. This indicates that cathode rays produce heating effect.
- (vi) They cause ionisation of the gas through which they pass.
- (vii) They produce X-rays when they strike against the surface of hard metals like tungsten, molybdenum etc.
- (viii) They produce green fluorescence on the glass walls of the discharge tube, as well as on certain other fluorescent substances such as zinc sulphide.
- (ix) They affect the photographic plates.
- (x) They possess penetrating effects (i.e., they can pass through thin foils of metals). They are stopped by only by the metals of greater thickness.

From the above-mentioned properties (important ones are highlighted in red), a conclusive statement can be made which is –

The negatively charged material particles constituting the cathode rays are called electrons. By measuring the amount of deflections Thomson was able to calculate the value of e/m of electrons = 1.758820×10^{11} C/kg. Hence, an electron is a fundamental sub-atomic particle which carries a unit negative charge and has a mass nearly equal to $1/1837^{\text{th}}$ of that of hydrogen atom.

Discovery of protons: study of anode rays

- Since the atom as a whole is electrically neutral and the presence of negatively charged particles in it was established therefore it was thought that some positively charged particles must also be present in the atom.
- For this purpose, Goldstein in 1886, performed discharge tube experiments in which he took perforated cathode and a gas at low pressure was kept inside the tube.
- On passing high voltage between the electrodes, it was found that some rays were coming from the side of the anode which passed through the holes in the cathode and produced green fluorescence on the opposite glass wall coated with zinc sulphide (ZnS).
- **These rays were called anode rays or canal rays or positive rays (because they were found to carry positive charge).**

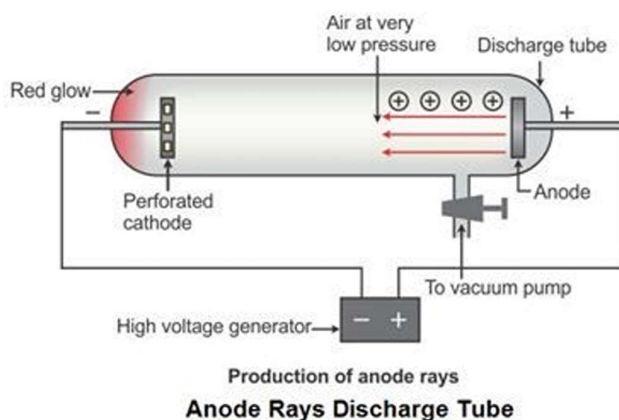


Figure 2. Experimental set-up of anode ray discharge tube.

PROPERTIES OF ANODE RAYS:

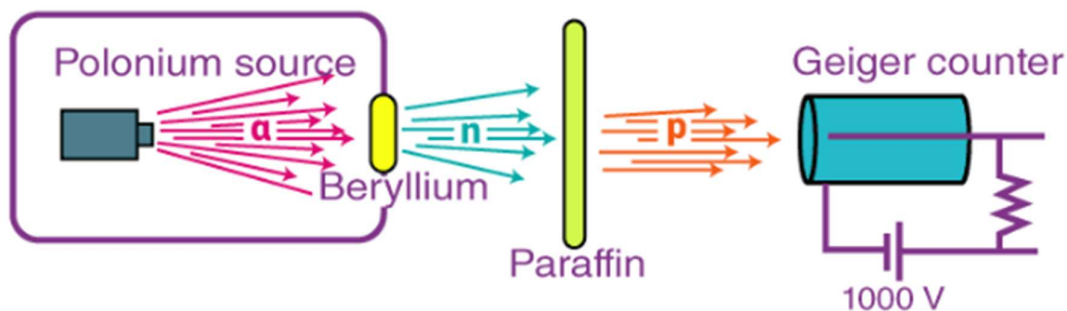
- (i) They travel in straight lines. However, their speed is much less than that of the cathode rays.
- (ii) That are made up of material particles
- (iii) They are positively charged, as indicated by the direction of deflection of these rays in the electric and magnetic fields. That is why they are called positive rays.
- (iv) Unlike cathode rays, the ratio, charge / mass (i.e. e/m) is found to be different for the particles constituting anode rays when different gases are taken inside the discharge tube. In other words, the value of e/m depends upon the nature of the gas taken inside the discharge tube.

- (v) The value of the charge (e) on the particles constituting the anode rays is also found to depend upon the nature of the gas taken inside the discharge tube.
- (vi) The mass (m) of the particles constituting the anode rays is also found to be different for different gases taken in the discharge tube- However, its value is found to be nearly equal to that of the atom of the gas.

Hence, a proton may be defined as a fundamental sub-atomic particle which carries one-unit positive charge and has a mass nearly equal to that of hydrogen atom.

Discovery of neutrons

- After the discovery of electron and proton, it was well established that atom is divisible and is made up of charged particles. This was further confirmed by the phenomenon of radioactivity, discovered by Becquerel 1986.
- Radioactivity is the phenomenon of spontaneous emission of radiations of certain elements like Uranium, radium etc. the elements emitting such radiations are called radioactive elements.
- He placed uranium salts on a wrapped photographic plate and exposed it to sunlight, expecting the uranium to absorb sunlight and emit X-rays. Even when the experiment was conducted on an overcast day and the uranium was not exposed to sunlight, the photographic plates were still exposed. He realized that the uranium was emitting some form of radiation spontaneously, without needing an external energy source like sunlight.
- James Chadwick fired alpha radiation at beryllium sheet from a polonium source. This led to the production of an uncharged, penetrating radiation.
- This radiation was made incident on paraffin wax, a hydrocarbon having a relatively high hydrogen content.
- The protons ejected from the paraffin wax (when struck by the uncharged radiation) were observed with the help of an ionization chamber.
- The range of the liberated protons was measured and the interaction between the uncharged radiation and the atoms of several gases was studied by Chadwick.
- He concluded that the unusually penetrating radiation consisted of uncharged particles having (approximately) the same mass as a proton. These particles were later termed 'neutrons'.



Discovery of neutron

Figure 3. Experimental set-up of neutrons.

THOMSON'S ATOMIC MODEL

J.J. Thomson, in 1904, proposed that an atom was a sphere of positive electricity in which were embedded number of electrons, sufficient to neutralize the positive charge. The stability of the atom was explained as a result of the balance between the repulsive forces between the electrons and their attraction towards the centre of the positive sphere. This model is compared with a water melon in which seeds are embedded or with a cake or pudding in which raisins (dried grape/kishmish) are embedded. That is why this model is sometimes called resin or plum pudding model. However, this model could not satisfactorily explain the results of scattering experiments, carried out by Rutherford in 1911 and was rejected.

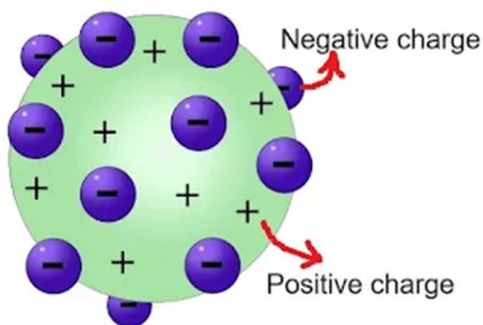


Figure 4. Thomson's atomic model.

RUTHERFORD'S MODEL (NUCLEAR MODEL) OF ATOM- DISCOVERY OF NUCLEUS

In 1909, Rutherford conducted particle scattering experiments. A fine stream of alpha particles bombards an extremely thin gold foil (0.004nm) in this experiment. Behind the gold foil is a

fluorescent screen (ZnS), on which points emerging from-particles were captured. Polonium was employed as the α -particles' source.

Rutherford's α -Scattering Experiment Observations

Rutherford conducted a series of tests utilising particle scattering by an extremely thin gold foil. The following observations were made:

- (i) The majority of the particles (99 percent) pass through it without deflection or deviation. (ii) Particles were deflected at tiny angles in several cases.
- (ii) Only a few particles were deflected by considerable angles,
- (iii) and one particle was deflected by 180° on rare occasions.

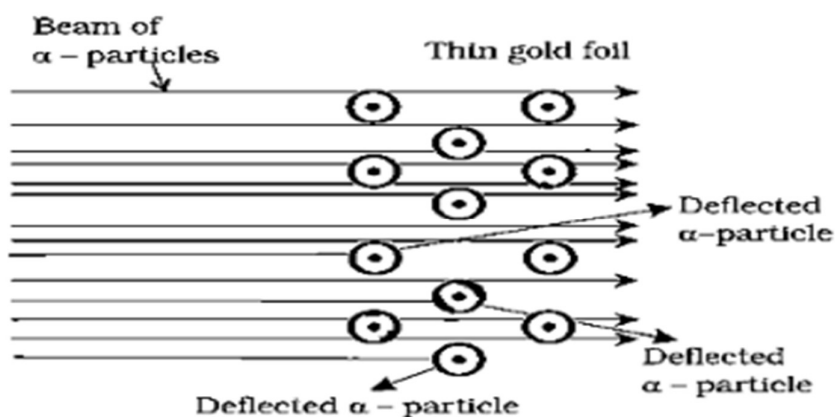


Figure 4. Pathways of the α -particles after colliding with the gold foil.

Conclusions of the experiment

- (i) Because most particles flowed through it without deflection, an atom must be exceedingly hollow and made up mostly of empty space.
- (ii) Only a few particles were deflected significantly. This means that: (a) Electrons cannot deflect heavy and positively charged particles due to their negative charge and low mass. (b) There must be an extremely hefty and positively charged body in the atom, such as the nucleus, that prevents positively charged particles from passing through. (c) Because the number of particles that experience 180° deflection is so small, the volume of a positively charged body must be a very small proportion of the atom's overall volume. This positively charged substance must be at the nucleus, which is the centre of the atom.

Rutherford's model of atom

- (i) At the centre of an atom lies a tiny positively charged nucleus, which is surrounded by a hollow region known as the extra nuclear part.
- (ii) Nucleons, which are made up of protons and neutrons, give the nucleus its positive charge, whereas electrons, which are found in the extra nuclear region, have minimal mass, and carry a negative charge.
- (iii) Because the number of electrons in the atom equals the number of protons, it is electrically neutral. As a result, the nucleus' total positive charge is balanced by the electrons' total negative charge.
- (iv) In the extranuclear section, electrons orbit the nucleus in circular routes known as orbits. As a result, an atom mimics the solar system, with the sun acting as the nucleus and the planets acting as circling electrons, and the model is referred to as the planetary model.
- (v) The electrostatic force of attraction holds electrons and nuclei together.
- (vi) Centrifugal forces perfectly balance the forces of attraction acting on the electron.

DRAWBACK OF RUTHERFORD'S ATOMIC MODEL

(i) Any charged entity in motion under the influence of attractive forces should radiate energy continually, according to classical mechanics. If this is the case, the electron will spiral and eventually fall into the nucleus, causing the structure to collapse. This type of behaviour is never seen. (ii) It contains no information on the electronic structure of atoms, such as how electrons are dispersed around the nucleus and their energies.

ATOMIC NUMBER AND MASS NUMBER

Atomic number (Z) The number of unit positive charges or protons contained in the nucleus of an element's atom is equal to the element's atomic number. It also represents the neutral atom's number of electrons. For example, the number of protons in Na is 11, hence the atomic number of Na is 11.

5.2 Mass number (A) The nucleons are the elementary particles (protons and neutrons) that make up the nucleus of an atom. An atom's mass number (A) is equal to the total of its protons and neutrons. It's always a number that's a whole number. As a result, the mass number (A) equals the sum of the number of protons (Z) and the number of neutrons (N). Therefore, number of neutrons (n) = Mass Number (A) – Number of protons (Z) $n = A - Z$

The general notation that is used to represent the mass number and atomic number of a given atoms is ${}^A_ZX$ where, X – symbol of element A - Mass number Z – atomic number.

Isotopes are same atomic number but differing mass number atoms of the same element. The discrepancy is due to the number of neutrons present. **Isobars** are atoms of various elements with distinct atomic numbers but the same mass numbers. **Isotones** are atoms of various elements that have the same number of neutrons. **Isoelectronic** refers to species (atoms or ions) that have the same number of electrons.

ELECTRONIC SPECTRA AND BOHR'S MODEL

- The **emission spectrum** of a chemical element or chemical compound is the spectrum of frequencies of electromagnetic radiation emitted due to electrons making a transition from a high energy state to a low energy state.
- It is observed that all elements give a characteristic spectrum which could not be explained with the help of Rutherford's model of atom.
- In order to understand line spectrum, it is essential to understand the nature of light (or radiant energy) which in turn was explained first with the help of 'Electromagnetic wave theory' and later with the help of 'Planck's Quantum Theory'.

NATURE OF ELECTROMAGNETIC RADIATION (ELECTROMAGNETIC WAVE THEORY)

This theory was proposed by James Clark Maxwell in 1864. The main points of this theory are-

- The energy is emitted from any source like the heated rod or filament of a bulb through which electric current is passed continuously in the form of radiations (or waves) and is called radiant energy.
- The radiations consist of electrical and magnetic fields oscillating perpendicular to each other and both perpendicular to the direction of the propagation of the light.
- The radiation possesses wave character and travel with the speed of light (3×10^8 m/s).
- These waves do not require any material or medium for propagation. For eg- rays coming from sun, that reach us directly through space without any medium.

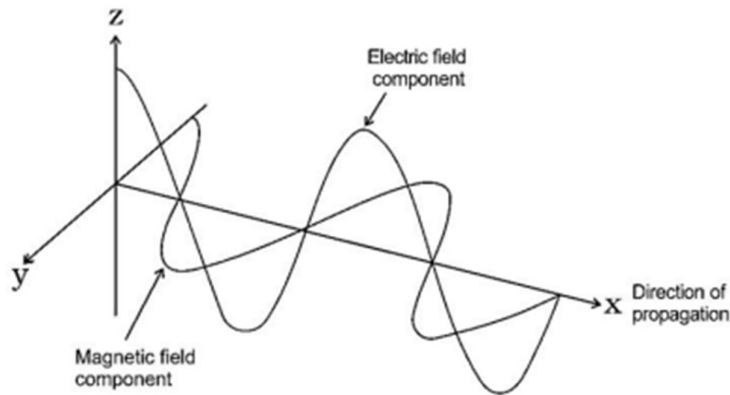


Figure 5. Radiation consisting of both electric and magnetic fields oscillating in the plane perpendicular to each other.

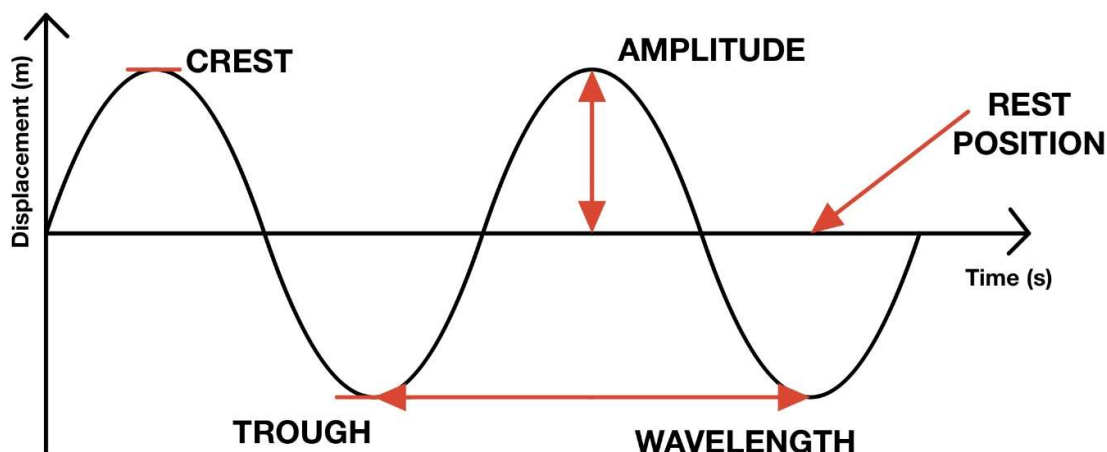
Some important characteristics of wave

The following are some of the characteristics of a wave:

- 1) **Amplitude:** The height of a wave's crest or trough (depth). Unit is metre (m)
- 2) **Frequency:** The number of waves that travel through a certain place in a second. Hertz (Hz) or s^{-1} are the units of measurement.
- 3) **Time Period:** A wave's period is the amount of time it takes to complete one vibration. time in seconds
- 4) **Velocity:** The velocity of a wave is the distance it travels in one second. m/s is the unit of speed. All types of electromagnetic radiation travel at the same speed in vacuum, which is 3×10^8 m/s. This is known as the speed of light.
- 5) **Wavelength (λ):** A wavelength is the distance between two consecutive crests or troughs. Angstrom($\text{\AA}$) [$1 \text{ \AA} = 10^{-10} \text{ m}$] is a unit of measurement.
- 6) **Wave Number:** This is the number of wavelengths per centimetre. m^{-1} is the unit of measurement. $\nu = 1 / \lambda$

Relationship between Velocity, Frequency & Wavelength

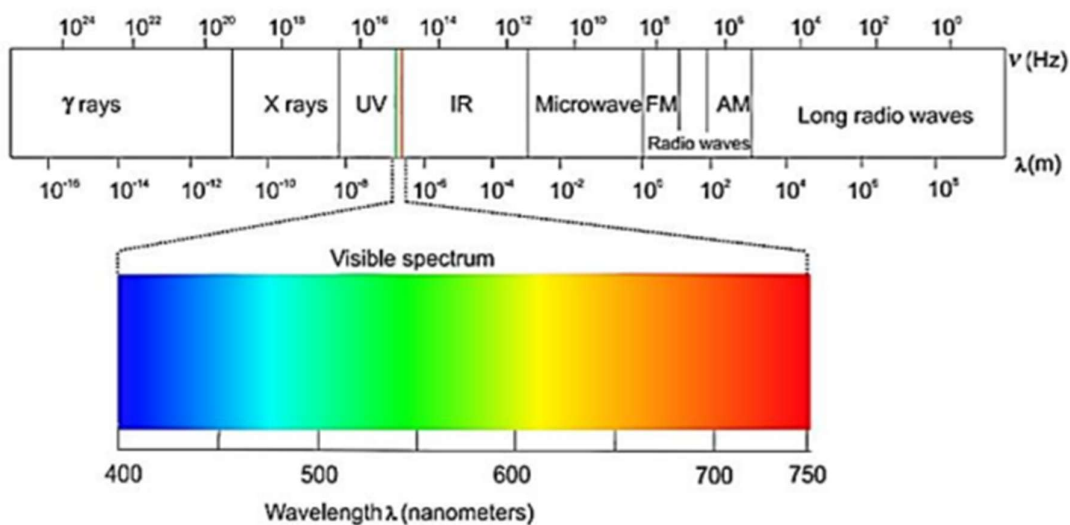
$c = \nu \lambda$. c: speed of light i.e. 3×10^8 m/s in vacuum ν : frequency; λ : wavelength



ELECTROMAGNETIC SPECTRUM: The different types of electromagnetic radiations differ only in their wavelength and hence frequencies. Their wavelengths increase in the following order-

Cosmic-rays < γ -rays < X-rays < Ultraviolet-Rays < Visible-rays < Infrared-rays < Microwaves < Radiowaves

When these electromagnetic radiations are arranged in order of their increasing wavelengths or decreasing frequencies, the complete spectrum obtained electromagnetic spectrum.



LIMITATIONS OF ELECTROMAGNETIC WAVE THEORY (PARTICLE NATURE OF ELECTROMAGNETIC RADIATION)

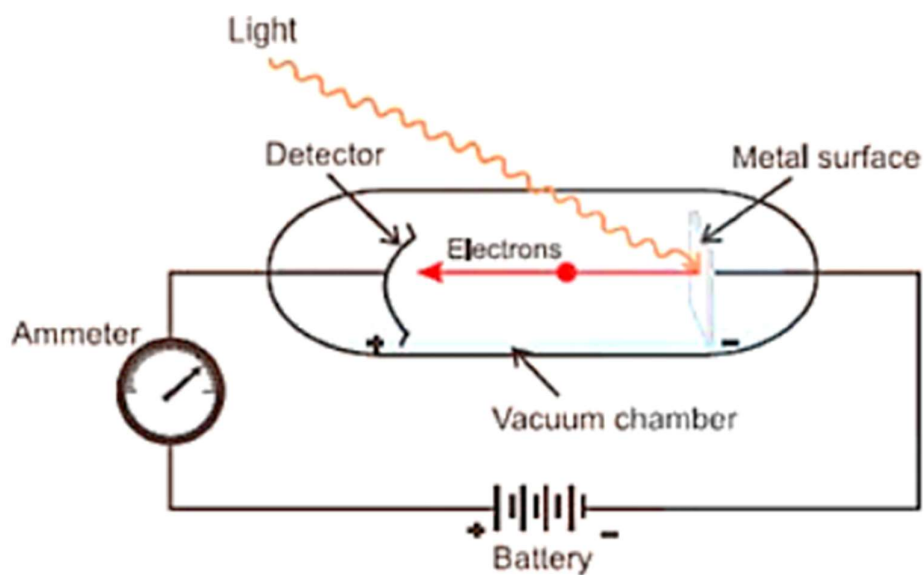
Electromagnetic wave theory was successful in explaining the properties such as interference, diffraction etc, but it could not explain the phenomena of black body radiation and photoelectric effect which could only be explained with the help of particle nature of matter. For instance, the electromagnetic wave theory is based on the continuous emission or absorption of the radiant energy, which cannot be used to explain black body radiations and photoelectric effect.

BLACK BODY RADIATIONS

- The first failure of the electromagnetic wave theory was observed in the form of black body radiations.
- According to Maxwell's theory of body heating, the intensity, or the amount of energy radiated per unit area, should grow without affecting the wavelength or frequency.
- However, we notice that when we heat an iron rod, it turns red, then white, and finally blue at extremely high temperatures. The frequency of radiated radiations is shifting because of this.
- **A black body is an ideal body that produces and absorbs radiation of all frequencies, and the radiation emitted by a black body is known as black body radiation.**
- When some solid substances are heated, the atom of the substance, are set into oscillation and emit radiation of frequency ν .
- Now as the heating is continued, more and more energy is being absorbed by the atoms and they emit radiations of higher and higher frequency.

PHOTOELECTRIC EFFECTS

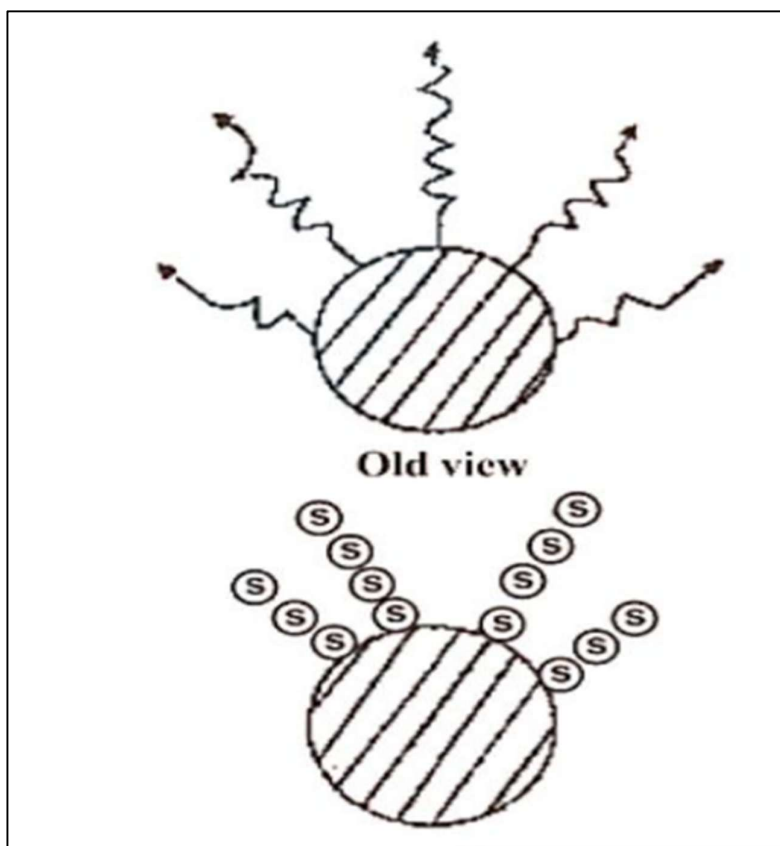
When radiations with a specific minimum frequency (ν_0) strike a metal's surface, electrons are expelled from the metal's surface. The photoelectric effect is the name for this phenomenon. Photoelectrons are the electrons that are released. According to Maxwell's Theory, electron ejection should be dependent on the intensity of radiation; if electrons are not ejected, raising the intensity will allow them to be ejected.



Following are some observations:

- (i) The electrons are ejected from the metal surface as soon as the light beam impacts it, i.e. there is no time lag between the light beam impacting the metal surface and the ejection of electrons.
- (ii) The intensity or brightness of light is related to the number of electrons ejected.
- (iii) There is a distinctive minimum frequency, ν_0 (also known as threshold frequency), below which no photoelectric effect is detected for each metal. The expelled electrons have a particular kinetic energy when the frequency is greater than zero. The kinetic energy of these electrons grows as the frequency of light utilised increases.

MAX PLANCK'S QUANTUM THEORY



The essential points of this theory are:

- (i) Energy is emitted or absorbed discontinuously in the form of small discrete packets of energy rather than constantly. A 'quantum' is the name given to each such energy packet. This quantum of energy is known as a photon in the case of light.
- (ii) Only one photon can be delivered to one electron or other particle at a time.
- (iii) It is impossible to divide or distribute a quantum.
- (iv) The frequency of radiation is precisely proportional to the energy of each quantum.
 $E = h\nu$ or $E = h\nu = hc/\lambda$ where, h = Planck's constant = 6.626×10^{-34} Js.
- (v) A body's total energy emitted or absorbed will be quantified in whole numbers. $E = nh\nu = nhc/\lambda$ This is also known as "energy quantisation."

Explanation of Photoelectric effect with the help of plank's theory

When a photon of a specific frequency strikes the surface of a metal atom, it imparts all its energy to the metal atom's electron. Only if the photon's energy is high enough to overcome the nucleus's attraction to the electron will the electron be ejected from the metal. As a result,

photoelectrons are only expelled when the input light has a minimal frequency (threshold frequency ν_0). The "Work Function," which is " $h\nu_0$," is the threshold energy necessary for emission. If the incident light's frequency (ν) exceeds the threshold frequency (ν_0), the surplus energy is transferred to the electron as kinetic energy.

$$\text{Energy of one quantum (} h\nu \text{)} = \text{Threshold Energy (} h\nu_0 \text{)} + \text{Kinetic Energy (} \frac{1}{2} m_e v^2 \text{)}$$

When, the number of quanta incident increases as the intensity increases, resulting in an increase in the number of photoelectrons expelled. When $\nu > \nu_0$, the energy of each photon increases, and consequently the kinetic energy of each ejected electron grows as the frequency is increased.

Note: Energy can also be expressed in Electron Volt(eV). The energy acquired by an electron when it is accelerated through a potential difference of one volt. $1\text{eV} = 1.602 \times 10^{-19} \text{ J}$.

STUDY OF SPECTRUM

A spectrum is a group of band or wavelengths/ colours and spectroscopy is the study of emission or absorption spectra.

There are two types of spectra- **(1) Emission spectrum and (2) Absorption spectrum.**

(1) Emission spectrum: When rays from a source strike a prism and are split into distinct wavelengths before being recorded on a photographic plate. When there are no pauses between wavelengths, and one merges into the next, then the resultant spectra obtained is called **continuous emission spectra**. **Discontinuous Emission Spectra**, also known as **Line Spectra** or **Atomic Spectra**, are a type of continuous emission spectrum. Certain wavelengths are missing from a group, leaving dark areas in between, causing the spectrum to be discontinuous. It's also known as an element's fingerprint. Line spectra are produced from a volatile salt placed in a flame.

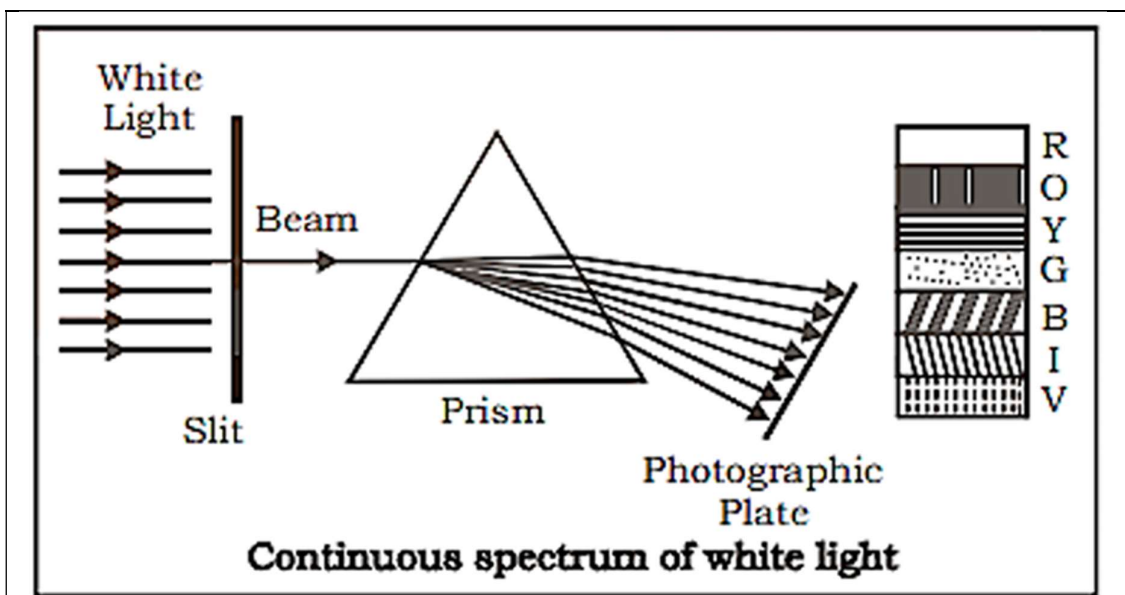


Figure: Continuous Emission Spectra of White Light

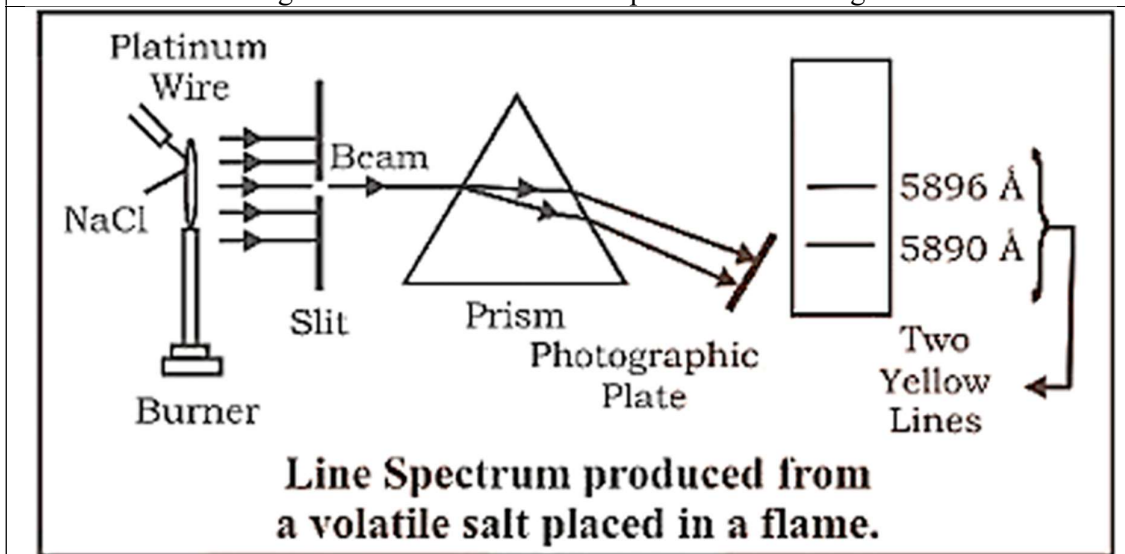
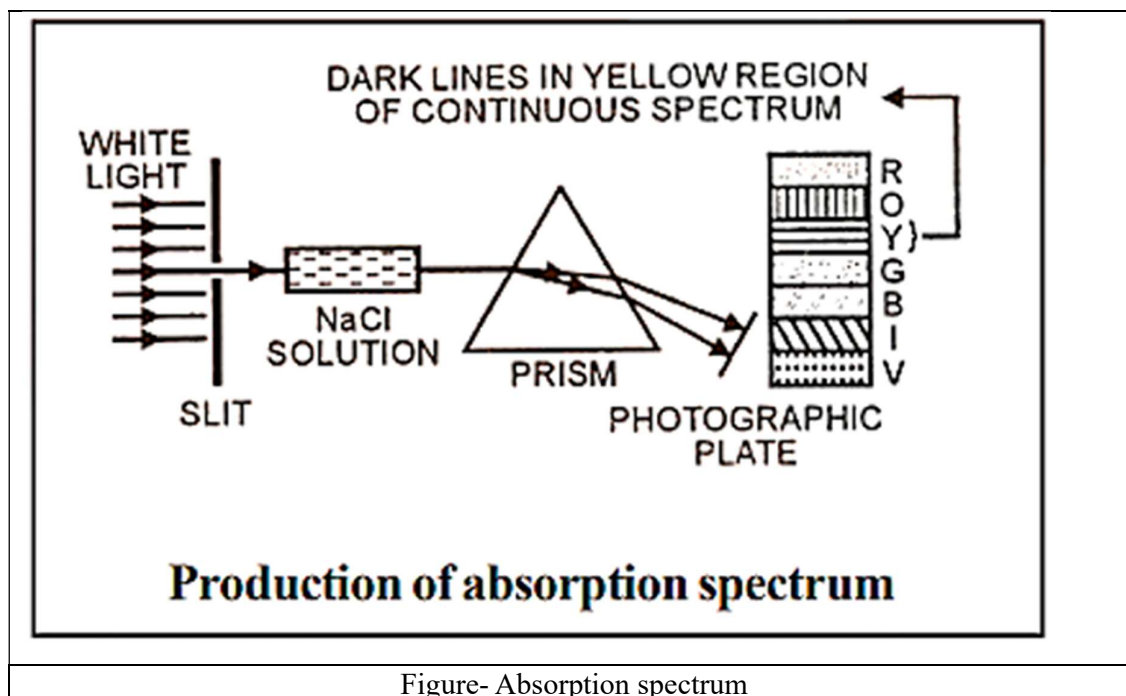


Figure: Discontinuous Emission Spectra of White Light

- (2) **Absorption Spectra:** When light from any source is first passed through the solution of a chemical substance and then analysed, it is observed that there are some dark lines in the otherwise continuous spectra. Bohr researched the atomic spectra of hydrogen and offered his hypothesis based on his findings.



Difference between Emission Spectrum and Absorption Spectrum

Emission Spectrum	Absorption Spectrum
1. Obtained when the radiation from the source is directly analysed in the spectroscopy.	1. Obtained when white light is first passed through a substance and the transmitted light is analysed in the spectroscopy.
2. Consists of bright coloured lines separated by dark spaces.	2. Consists of dark lines in the otherwise continuous spectrum.
3. Can be continuous (if source emits white light) or discontinuous, i.e., line spectrum (if source emits some coloured radiation).	3. Always discontinuous spectrum consisting of dark lines.

Line Spectrum of Hydrogen

The H_2 molecules breakdown when an electric discharge is transmitted through gaseous hydrogen, and the energetically excited hydrogen atoms that result generate discrete frequency electromagnetic radiations. Several lines in the hydrogen spectra are named after their discoverer. Because the energy of an electron cannot change continuously but can only have fixed values, we get discrete lines rather than a continuous spectrum. As a result, the energy of one electron can be quantified.

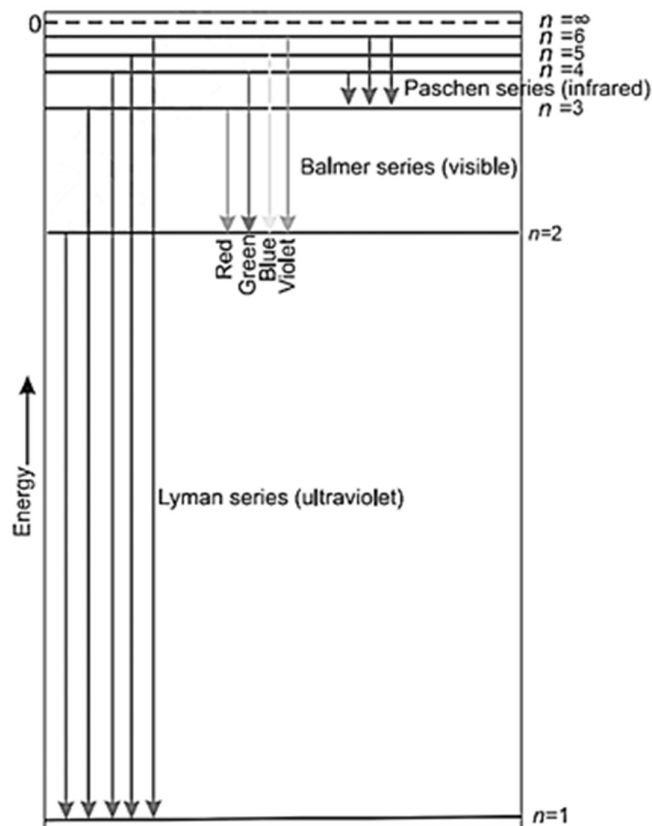
LYMAN Series: When an electron jumps from one of the higher states to the ground state or first state ($n = 1$), a series of ultra violet spectral lines is generated, which is known as the Lyman series. As a result, according to Rydberg's formula, $n_1 = 1$, $n_2 = 2, 3, 4, 5 \dots$

BALMER Series: When an electron goes from a higher state to a state with $n=2$, a series of spectral lines called the Balmer series is emitted in the visible range. As a result, according to Rydberg's formula, $n_1 = 2$, $n_2 = 3, 4, 5, 6 \dots$

PASCHEN Series: When an electron moves from one of the higher states to the $n=3$ state, a series of infrared spectral lines is generated, known as the Paschen series. As a result, $n_1 = 3$ and $n_2 = 4, 5, 6$ in Rydberg's formula.

BRACKETT Series: When an electron moves from one of the higher states to the state with $n = 4$, it emits a series of infrared spectral lines known as the Brackett series. As a result, according to Rydberg's formula, $n_1 = 4$, and $n_2 = 5, 6, 7 \dots$

PFUND Series: When an electron goes from one of the higher states to the one with $n = 4$, it emits a series of infrared spectral lines known as the Pfund series. The formula of Rydberg is $n_1 = 5$ and $n_2 = 6, 7 \dots$



BOHR'S MODEL OF ATOM

Bohr researched the atomic spectra of hydrogen and offered his hypothesis based on his findings. The postulates are

(1) An atom is made up of a small, heavy, positively charged nucleus at the centre, which is surrounded by electrons in circular orbits.

(2) Electrons can only revolve in orbits with a predetermined energy value. As a result, these orbits are referred to as "energy levels" or "stationary states." 1,2,3,... are the numbers assigned to them. Principal Quantum Numbers are the names given to these numbers.

(a) An electron's energy is given by: $E = -R_H (Z^2 / n^2)$ $n = 1, 2, 3, \dots$

R_H is Rydberg's constant and its value is 2.18×10^{-18} J. Z = atomic number

$$E_n = -2.18 \times 10^{-18} \left(\frac{Z}{n}\right)^2 \text{ J/ atom}$$

$$E_n = -13.6 \times 10^{-18} \left(\frac{Z}{n}\right)^2 \text{ eV/ atom}$$

$$E_n = -1312 \times 10^{-18} \left(\frac{Z}{n}\right)^2 \text{ KJ/ mol}$$

As a result, the energies of various levels are arranged in the following order: K L M N..... and so on. **The energy of the lowest state ($n=1$) is referred to as ground state energy.**

(b) **Stationary state radius:** $r_n = 52.9 \left(\frac{n}{Z}\right)^2 \text{ pm}$

The radius of the first stationary state for an H-atom ($Z = 1$) is known as the Bohr orbit (52.9 pm)

(c) Electron velocities in different orbits: $2.188 \times 10^2 / n \text{ ms}^{-1}$.

(3) Because electrons can only rotate in orbits with fixed energy values, electrons in an atom can only have certain energy values and not any of their own. An electron's energy is so quantified.

(4) An electron in an atom's angular momentum, like its energy, can take on specific definite values and not any value at all.

$$mvr = nh/2\pi$$

(5) When an electron is present in the same shell, it does not lose or gain energy.

(6) When an electron obtains energy, it is excited to higher energy levels, and when it loses energy in the form of electromagnetic radiations, it is de-excited and returns to lower energy levels.

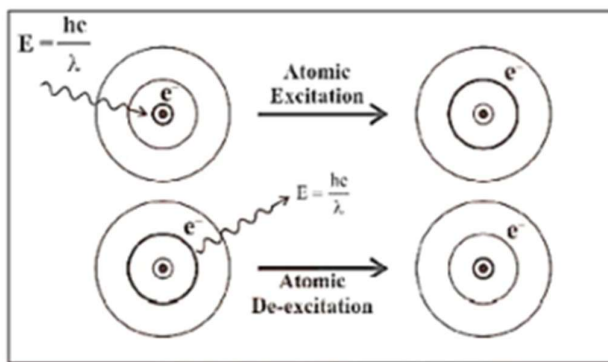


Figure: Excitation by absorption of light and de-excitation by emission of light

What does negative energy in the case of the hydrogen atom imply?

The energy of an electron in an atom is lower than the energy of a free electron at rest, as shown by the negative sign. The energy value of a free electron at rest is zero since it is infinitely far away from the nucleus ($n = \infty$). E_n becomes increasingly negative as the electron approaches closer to the nucleus (as n decreases). $n=1$ corresponds to the most stable orbit and has the largest negative energy value. Note: Bohr's model is applicable to H-atom or H-like species like He^+ , Li^{2+} , Be^{3+}

$$\Delta E = E_f - E_i$$

$$\Delta E = \left[-\frac{R_H}{n_f^2} \right] - \left[-\frac{R_H}{n_i^2} \right]$$

$$\Delta E = R_H \left[\frac{1}{n_i^2} - \frac{1}{n_f^2} \right] = 2.18 \times 10^{-18} \left[\frac{1}{n_i^2} - \frac{1}{n_f^2} \right] \text{ J/atom}$$

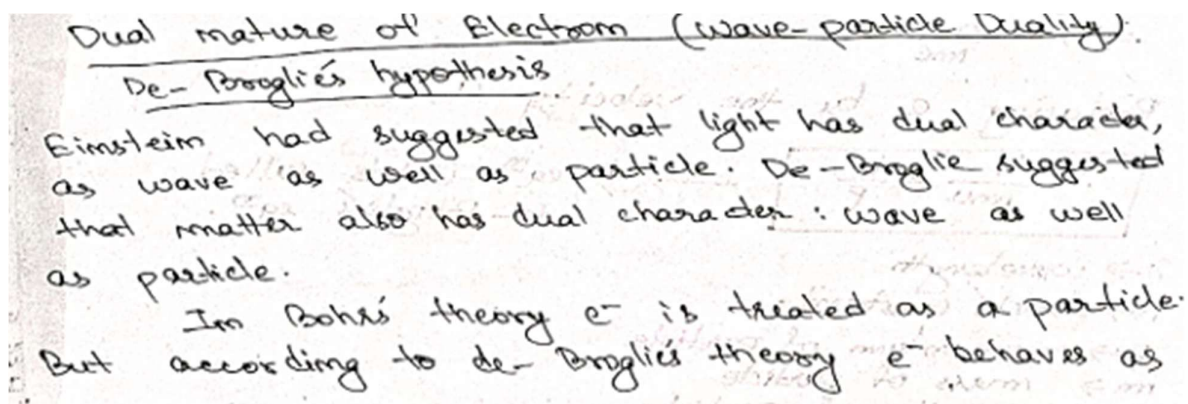
The wavelength associated with the photon's absorption or emission is:

$$\frac{1}{\lambda} = \frac{\Delta E}{hc} = \frac{R_H}{hc} \left[\frac{1}{n_i^2} - \frac{1}{n_f^2} \right] = 1.09677 \times 10^7 \left[\frac{1}{n_i^2} - \frac{1}{n_f^2} \right] \text{ m}^{-1}$$

Rydberg's formula is what it's called.

Limitations of Bohr's Model:

- (1) Inability to explain multi-electron atom line spectra.
- (2) It fails to account for the hydrogen spectra's finer characteristics (doublet-two closely spaced lines).
- (3) Inability to explain line splitting in the magnetic (Zeeman Effect) and electric (Stark Effect) fields- When a source generating radiation is placed in a magnetic or electric field, each spectral line splits up into a number of lines. The Zeeman Effect is the splitting of spectral lines in a magnetic field, while the Stark Effect is the splitting of spectral lines in an electric field.
- (4) It could not account for atoms' ability to form molecules through covalent connections.
- (5) He ignores matter's dual behaviour and contradicts the Heisenberg uncertainty principle.



a material ~~wave~~ ^{particle} as well as wave. He derived an expression for calculating the wavelength λ associated with a motion of a particle of mass m moving with velocity u according to which $\lambda = h/mu$ where h is planck's constant.

Derivation of de-Broglie's equation

The De-Broglie's equation for the wave-particle duality of e can easily be derived by using Einstein's mass-energy relationship.

By Einstein's mass-energy relation,

$$E = mc^2 \quad \text{--- (i)}$$

By planck's eqⁿ,

$$E = h\nu \quad \text{--- (ii)}$$

equating (i) and (ii)

$$h\nu = mc^2 \quad \text{--- (iii)}$$

$$\therefore \nu = \frac{c}{\lambda} \quad \text{--- (iv)}$$

Putting the value of (iv) in (iii)

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

$$\Rightarrow \lambda = \frac{h}{mc}$$

Replacing c by the velocity u ,

$$\boxed{\lambda = \frac{h}{mu} = \frac{h}{p}} \quad \text{--- (v)} \quad \text{eqⁿ (v) is called de-Broglie's eqⁿ.}$$

$\lambda \rightarrow$ wavelength

$h \rightarrow$ planck's constant.

$p \rightarrow$ momentum of particle

$m \rightarrow$ mass of particle

$u \rightarrow$ velocity of particle

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

$$\Rightarrow \boxed{\lambda \propto \frac{1}{p}}$$

Momentum of the moving particle is inversely proportional to its wavelength.

Let the KE of the particle of mass m is E .

$$E = \frac{1}{2}mv^2$$

$$\Rightarrow 2E = mv^2$$

$$\Rightarrow 2mE = m^2v^2$$

$$\Rightarrow mv = \sqrt{2mE}$$

$$\Rightarrow p = \sqrt{2mE}$$

From De-Broglie's eqⁿ

$$\boxed{\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}}$$

Davidson and Germer made the following modification

In de-Broglie's eqⁿ

$$\frac{1}{2}mv^2 = eV$$

$$\Rightarrow mv^2 = 2eV$$

$$\Rightarrow mv = \sqrt{2meV}$$

$$\Rightarrow \lambda = \frac{h}{mv} = \frac{h}{\sqrt{2meV}}$$

$$= \frac{6.626 \times 10^{-34} \text{ Js}}{\sqrt{2(9.109 \times 10^{-31} \text{ kg})(1.602 \times 10^{-19} \text{ C})}}$$

$$= 12.26 \times 10^{-10} \text{ m}$$

WAVE NATURE OF MATTER

Wave nature of electron and quantisation of angular momentum

Consider an electron moving in a circular orbit around a nucleus. Evidently if the wave is to remain continually in phase, the circumference of the circle must be integral multiple of the wave length λ , i.e.,

$$\text{Circumference} = n\lambda$$

$$2\pi r = n\lambda = \frac{nh}{mu}$$

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

$$\Rightarrow mvr = nh/2\pi$$

Heisenberg's Uncertainty Principle

At the principle it is not possible to determine precisely both the posⁿ and momentum of a moving minute particle. The principle is mathematically expressed as-

$$(\Delta p) \cdot \Delta x \geq h/4\pi$$

where Δx = uncertainty with regard to the posⁿ
 Δp = " " " " " momentum
of the particle.

If Δx is very small, i.e., the posⁿ of particle is known more or less exactly Δp would be large

* Operator

→ The operation or pre-defined operation carried out on the function, which changes the old function into a new function or a constant value.

→ In Quantum Mech, operators are denoted by $(\hat{\ })$.

for eg $\Rightarrow \hat{A} = \frac{d}{dx}$

$$f(x) = x^2,$$

then

$$\hat{A}f(x) = \frac{d}{dx} x^2 = 2x \rightarrow \text{new } f(x)$$

operator

old $f(x)$

$$\text{eg} \Rightarrow \hat{A} = \frac{d}{dx}$$

$$f(x) = 4x$$

$$\hat{A}f(x) = \frac{d}{dx} 4x = 4 \rightarrow \text{constant value.}$$

operator

old $f(x)$

* Properties of operators

① Operators are directional in nature.

$$\frac{d}{dx} = \text{no meaning} \quad \hat{A} \frac{d}{dx} f(x) = \checkmark$$

L.H.S = operator

R.H.S = $f(x)$

operator = Left $\rightarrow$ right.

② Operators are meaningless without functions.

③ Operators in quantum mechanics must be linear.

and for an operator to be linear, it must satisfy the following condⁿ -

$$\hat{A} \rightarrow \text{operator} \quad f(x) = f(x) \quad g(x) = \text{another } f(x) \quad c \rightarrow \text{const.}$$

$$\hat{A} cf(x) = c \hat{A} f(x) \quad (\text{No const. No bahar kr de usay linear operator kehete hain}).$$

$$\textcircled{2} \hat{A} [f(x) + g(x)] = \hat{A} f(x) + \hat{A} g(x).$$

Any of two condⁿ is satisfied, then operator is linear.

① satisfied, then ② is also satisfied and vice versa.

eg $\rightarrow$ ① $\hat{A} = \frac{d}{dx}$ $f(x) = 4x^2$

$$\hat{A} f(x) = \frac{d}{dx} 4x^2 = 4 \frac{d}{dx} x^2 = 4 \times 2x = 8x.$$

$$\hat{A} f(x) = c \hat{A} f(x)$$

$\frac{d}{dx}$ is linear operator.

② $f(x) = 3x^2$

$g(x) = x^2$

$f(x) + g(x) = 4x^2.$

$\hat{A} = \frac{d}{dx}$

$$\hat{A} [f(x) + g(x)] = \frac{d}{dx} [3x^2 + x^2] = \frac{d}{dx} 3x^2 + \frac{d}{dx} x^2 = 6x + 2x = 8x.$$

$$\frac{d}{dx} 4x^2 = 8x.$$

$$\therefore \frac{d}{dx} \boxed{\hat{A} f(x) + \hat{A} g(x) = \hat{A} [f(x) + g(x)]}$$

$\frac{d}{dx}$ is linear operator.

Que whether the integration operator is linear or not ???

Yes. ① $\int c f(x) dx = c \int f(x) dx$

② $\int \{f(x) + g(x)\} dx = \int f(x) dx + \int g(x) dx$

Que square and $\sqrt{\quad}$ are linear operator ???

No.

Ques Is $\log$ a linear operator?

Solⁿ $\log(3) + \log(3) \neq \log(3+3)$
 $\log(2 \times 3)$

Say, $f(x) = 4x^2$.

then, $\log(4x^2) \neq \hat{A} \log(x^2)$

$\log 4 + \log x^2$

$\therefore \log$ is not a linear operator.

Q4 Property :- n^{th} power of an operator means operator is operated n^{th} times.

Say, $\hat{A} \rightarrow$ operator.

$f(x) \rightarrow$ arbitrary function.

$\hat{A}^n f(x) \rightarrow \hat{A} \rightarrow$ operated n times.

If $\hat{A} = \left(\frac{d}{dx} + x \right)$, then find the value of $\hat{A}^2$.

$\hat{A}^2 = \left(\frac{d}{dx} + x \right)^2 = \frac{d^2}{dx^2} + x^2 + 2x \frac{d}{dx} \rightarrow \text{WRONG}$

Let $f(x)$ be an arbitrary function.

then, $\hat{A}^2 f(x) = \left(\frac{d}{dx} + x \right)^2 f(x)$

$= \left(\frac{d}{dx} + x \right) \left(\frac{d}{dx} + x \right) f(x)$

$= \left(\frac{d}{dx} + x \right) \left[\frac{d f(x)}{dx} + x f(x) \right]$

$= \frac{d}{dx} \left[\frac{d f(x)}{dx} + x f(x) \right] + x \left[\frac{d f(x)}{dx} + x f(x) \right]$

$= \frac{d^2 f(x)}{dx^2} + x \frac{d f(x)}{dx} + f(x) \frac{dx}{dx} + x \frac{d f(x)}{dx} + x^2 f(x)$

$= \frac{d^2}{dx^2} f(x) + 2x \frac{d f(x)}{dx} + f(x) + x^2 f(x)$

$$= \left(\frac{d^2}{dx^2} + 2x \frac{d}{dx} + 4x^2 \right) f(x)$$

$$\therefore \hat{A}^2 f(x) = \left(\frac{d^2}{dx^2} + 2x \frac{d}{dx} + 4x^2 \right) f(x)$$

Que If $\hat{A} = \left(\frac{d}{dx} - x \right)$. Find $\hat{A}^2$.

$f(x)$ = be any arbitrary function.

$$\hat{A} f(x) = \left(\frac{d}{dx} - x \right) f(x)$$

$$\hat{A}^2 f(x) = \left(\frac{d}{dx} - x \right)^2 f(x) = \left(\frac{d}{dx} - x \right) \left(\frac{d}{dx} - x \right) f(x)$$

$$= \left(\frac{d}{dx} - x \right) \left[\frac{df(x)}{dx} - x f(x) \right]$$

$$= \frac{d}{dx} \left[\frac{df(x)}{dx} - x f(x) \right] - x \left[\frac{df(x)}{dx} - x f(x) \right]$$

$$= \left[\frac{d^2}{dx^2} - 1 - 2x \frac{d}{dx} + x^2 \right] f(x)$$

$$\therefore \hat{A}^2 = \frac{d^2}{dx^2} - 2x \frac{d}{dx} - 1 + x^2$$

Property - (5) To every observable in classical mechanics there exist an operator in quantum mechanics.

What are observables?

These are dynamic variables like posⁿ, momentum, kinetic energy, potential energy, angular momentum etc.

Dynamic variables $\rightarrow$ variables whose value change with motion.

OBSERVABLE	OPERATOR	OPERATION.
① position x, y, z .	$\hat{x}, \hat{y}, \hat{z}$	Multiplication. $\hat{x}f(x) = x \cdot f(x)$; $\hat{x}f(y) = x \cdot f(y) \dots$
② Potential energy. V_x, V_y, V_z	$\hat{V}_x, \hat{V}_y, \hat{V}_z$	Multiplication. $\hat{V}_x f(x) = V \cdot f(x)$; $\hat{V}_x f(y) = V \cdot f(y) \dots$
③ Momentum (linear) $P = mv$. $P_x = mv_x$ $P_y = mv_y$ $P_z = mv_z$	$\hat{P}_x = -i\hbar \frac{\partial}{\partial x} = \frac{h}{i} \frac{\partial}{\partial x}$ $= \frac{h}{2\pi i} \frac{\partial}{\partial x}$ $\hat{P}_y = -i\hbar \frac{\partial}{\partial y}$ $\hat{P}_z = -i\hbar \frac{\partial}{\partial z}$	$\hat{P}_x f(x) = -i\hbar \frac{\partial}{\partial x} f(x)$ <div style="text-align: center;">↓ Partial derivative w.r.t x then multiplication by $-i\hbar$.</div>

GATE eg $\rightarrow f(x) = e^{ikx}$ $\hat{P}_x$

$$\hat{P}_x f(x) = -i\hbar \frac{\partial}{\partial x} e^{ikx}$$

$$= -i\hbar (ik e^{ikx})$$

$$= -i^2 k\hbar e^{ikx} = k\hbar e^{ikx}$$

$$= \frac{h\hbar}{2\pi} e^{ikx}$$

④ Kinetic energy
 $K.E = \frac{1}{2}mv^2$

$$\hat{T} = \frac{\hat{P}^2}{2m}$$

$$\hat{T}_x = \frac{\hat{P}_x^2}{2m} = \frac{(-i\hbar \frac{\partial}{\partial x})^2}{2m}$$

$$\hat{T}_y = \frac{\hat{P}_y^2}{2m}$$

$$\hat{T}_z = \frac{\hat{P}_z^2}{2m}$$

$$\therefore \hat{T}_x = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

⑤ operator for total energy

Total energy $\Rightarrow E = K.E + P.E$

Hamiltonian operator $\leftarrow \hat{H} = \hat{T} + \hat{P}$

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} \right) + \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} \right) +$$

$\hat{V}_{xyz}$

$$\hat{H} = -\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] + \hat{V}_{xyz}$$

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \hat{V}_{xyz}$$

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \nabla^2 = \text{laplacian operator.}$$

Eigenvalue and Eigen function:

$\hat{A} \rightarrow$ any operator for observable.

$\psi \rightarrow$ any wave fⁿ.

then, $\boxed{\hat{A}\psi = \lambda\psi}$ $\rightarrow$ this type of function is called eigen function.

λ
 $\downarrow$
eigen value.

This λ is called eigenvalue eqⁿ.

If after the operation of an operator, a function doesn't lose its identity giving a const. value, attached with it. The const. value is known as eigenvalue, the fⁿ is known as eigen-fⁿ.

$$\rightarrow \hat{A} = 100 \frac{d}{dx} \quad \psi = e^{2x}$$

$$100 \frac{d}{dx} e^{2x} = 200 e^{2x}$$

↓
eigen value.

$$\rightarrow \hat{A} = \frac{d}{dx} \quad \psi = 100 e^{2x}$$

$$\frac{d}{dx} 100 e^{2x} = \textcircled{2} 100 e^{2x}$$

↓
eigen value.

Orthogonal wave functions.

$\vec{A}$ and $\vec{B}$ are two vectors, then

$$\vec{A} \cdot \vec{B} = |\vec{A}| |\vec{B}| \cos \theta$$

$$\theta = 90^\circ, \cos 90^\circ = 0$$

$$\therefore \vec{A} \cdot \vec{B} = 0 \rightarrow \vec{A} \text{ and } \vec{B} \text{ are orthogonal to each other.}$$

In Quantum $\rightarrow$ wave $\psi \rightarrow$ vector quantities.

$$\vec{\psi}_m \cdot \vec{\psi}_n = 0$$

$\rightarrow \psi_m$ and ψ_n are orthogonal to each other.

In Quantum written as

$$\int \psi_m^* \psi_n d\tau = 0$$

$\rightarrow \psi_m$ and ψ_n are orthogonal to each other.

$$\int \psi_m^* \psi_n d\tau = 0 \quad \text{or} \quad \int \psi_n \psi_m^* d\tau = 0$$

* $\rightarrow$ complex conjugate.

In Quantum, orthogonal means independent.
as in ENR, $\vec{B}$ & $\vec{E}$ are independent to each other.

* Degenerate and non-degenerate eigen-pts

If ψ_m and ψ_n are eigen-pts of operator $\hat{A}$.

$$\hat{A} \psi_m = a_m \psi_m$$

$$\hat{A} \psi_n = a_n \psi_n$$

Case (i)

If $a_m = a_n$, then ψ_m and ψ_n are degenerate eigen-pts and a_m and a_n are degenerate eigen-value.

Case (ii) ↓

If $a_m \neq a_n$, then ψ_m and ψ_n are non-degenerate eigen-pts and a_m and a_n are non-degenerate eigen value.

eg → $\begin{array}{|c|c|c|} \hline 1 & 1 & 1 \\ \hline p_x & p_y & p_z \end{array} \rightarrow \text{degenerate states of energy}$
But why??

$$\text{When } \hat{H} \psi_{2p_x} = E_{2p_x} \psi_{2p_x}$$

$$\hat{H} \psi_{2p_y} = E_{2p_y} \psi_{2p_y}$$

$$\hat{H} \psi_{2p_z} = E_{2p_z} \psi_{2p_z}$$

found that $E_{2p_x} = E_{2p_y} = E_{2p_z}$.
This are degenerate energy states.

non-degenerate eg → (s) and (p) orbital.

$$* [x^2, p_x^2] = ??$$

$$[x^2, \hat{p}_x \hat{p}_x] = [x^2, \hat{p}_x] \hat{p}_x + \hat{p}_x [x^2, \hat{p}_x]$$

$$= i\hbar 2x \hat{p}_x + \hat{p}_x i\hbar 2x$$

$$= 2i\hbar x \hat{p}_x + 2i\hbar \hat{p}_x x \rightarrow \text{CORRECT}$$

$$= 4i\hbar x \hat{p}_x \rightarrow \text{WRONG}$$

$$= 2i\hbar (\hat{x} \hat{p}_x + \hat{p}_x \hat{x})$$

$$\therefore \hat{x} \hat{p}_x \neq \hat{p}_x \hat{x} [\because \hat{x} \text{ and } \hat{p}_x \text{ do not commute}]$$

* Normalisation and Probability

A/Max Born interpretation of wave function, a wave function does not determine the exact location of a microscopic particle. However, it gives probability of finding the particle in desired region by the expression.

$$P = \int_a^b \psi \psi^* d\tau$$

a to b $\rightarrow$ desired region

$$\begin{aligned} d\tau &= dx dy dz \rightarrow 3D \\ &= dx dy \rightarrow 2D \\ &= dx \rightarrow 1D \end{aligned}$$

Probability is not for a point, but is for a region.

$$\text{Probability density} = |\psi \psi^*| = |\psi|^2$$

Total probability in a region = 1

$$\int_a^b \psi \psi^* d\tau = 1$$

$\rightarrow$ then ψ is said to be normalised wave fn.

If ψ is not normalised, then we must have to normalise it.

Ques Normalise the wave fn, $\psi = x$ betⁿ 0 to 1

$$\int_a^b \psi \psi^* d\tau = 1$$

$$\int_0^1 x x dx = 1$$

$$\Rightarrow \int_0^1 x^2 dx = 1$$

$$\Rightarrow \frac{1}{3} \neq 1$$

$\psi = x$ not normalised.

$\frac{1}{3} \rightarrow$ reciprocal $\rightarrow 3 \rightarrow$ SQRT $\rightarrow \sqrt{3} \rightarrow$ multiply $\downarrow$
 $\psi = \sqrt{3}x$ normalised

ly, if an attempt is made to measure exactly the velocity of particle the uncertainty with regard to pos^2 will become large. The physical concept of the uncertainty principle may become clear when it is realised that all observations have to be made by impact of light radiations (photons). If the object is of reasonable size, its pos^2 or vel. will not be altered by the impact of light photons. Hence, it will be impossible to know precisely the position & the vel. of the object, i.e. the uncertainty Δx or Δp would be negligible. But this can't be so when the object is extremely minute, such as an e^- moving say, in a circular path. It will suffer a change in its vel. and path due to the impact of even a single photon of light used to observe it.

In view of the uncertainty principle, Bohr's model in which e^- are considered as particles revolving in definite orbits with definite velocities become untenable. It is not possible to know exactly the pos^2 of an e^- moving with a particular velocity as in Bohr model. Instead it is possible only to state or predict the probability of locating an e^- moving with a particular velocity in a given region of space around the nucleus at a given time.

The concept of an e^- following a definite orbit where its pos^2 and velocity are known exactly must therefore be replaced by the probability of finding an e^- in particular pos^2 or in particular vol ^{2} of space. The Schrodinger wave eq ^{n} provides a satisfactory description of atom in these terms. Sol ^{n} of these wave eq ^{n} are called wave fun ^{n} and the symbol is ψ . The probability of finding a e^- in space whose coordinates are x, y, z is $\psi^2(x, y, z)$.

Schrödinger Wave equation

It is evident that e^- behaves as particles as well as matter wave. If the e^- behaves as a wave there must be a wave equation to describe their behaviour. Schrödinger in 1926 gave a wave ~~eqⁿ~~ behaviour of e^- in atoms and molecules. In Schrödinger wave ~~eqⁿ~~ ^{model} of atom, the discrete energy levels or orbits proposed by Bohr are replaced by mathematical fm ψ which are related with the probability of finding the e^- at various places around the nucleus.

Schrödinger used the classical time independent wave eqⁿ to describe the particle wave substituting de-Broglie's relation for λ .

If an e^- is considered as a wave which moves only in 1D, then

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} \psi \quad (i)$$

An e^- may move in 3-D x, y, z so eqⁿ (i) takes the form,

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2} \psi \quad (ii)$$

From de-Broglie's eqⁿ,
 $\lambda = \frac{h}{mu}$

$$\therefore (ii) \Rightarrow \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2 m^2 u^2}{h^2} \psi$$

$$\Rightarrow \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{4\pi^2 m^2 u^2}{h^2} \psi = 0 \quad (iii)$$

$$E = K + V$$

$$\Rightarrow K = E - V$$

$$\Rightarrow \frac{1}{2} m u^2 = E - V$$

$$\Rightarrow u^2 = \frac{2(E - V)}{m} \quad (iv)$$

Putting the value of (iv) in (iii).

$$\therefore (iii) \Rightarrow \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2\pi^2 m^2 (E - V)}{mh^2} \psi = 0$$

$$\Rightarrow \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m^2 (E - V)}{mh^2} \psi = 0$$

$$\Rightarrow \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m (E - V)}{h^2} \psi = 0$$

$$\Rightarrow \left[\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \right] \quad (v)$$

This is known as Schrodinger's wave eqⁿ in 3-D.

eqⁿ (v) can be written as,

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

∇^2 is known as Laplacian mathematical operator.

now, $\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$

$$\Rightarrow \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = - \frac{8\pi^2 m}{h^2} (E - V) \psi$$

$$\Rightarrow \frac{-h^2}{8\pi^2 m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) = (E - V) \psi$$

$$\Rightarrow \frac{-h^2}{8\pi^2 m} (\nabla^2 \psi) = (E - V) \psi$$

$$\Rightarrow \left(\frac{-h^2}{8\pi^2 m} \nabla^2 + V \right) \psi = E \psi$$

$$\Rightarrow \boxed{\hat{H} \psi = E \psi}$$

$\hat{H}$ = Hamiltonian operator

Derivation of Schrödinger wave eqⁿ

From Book

Puri - Sharma - Kalia

Operators

From Book

Puri - Sharma - Kalia

R.K - Prasad - Ch-3

The Schrödinger wave eqⁿ, being a 2nd order diff. eqⁿ, has innumerable solⁿ, many of them having no significance at all. Out of these, only those solⁿ are significant which gives certain definite and acceptable values of the total energy E . The acceptable value of total Energy E given by a solⁿ is called eigenvalue and the corresponding function ψ which gives the eigenvalue of the Energy is called eigenfunction. Thus every function is not an eigen (acceptable) function.

Conditions to be satisfied by an eigen (or acceptable wave fn)

1. The wave function must be finite: an infinite value of ψ at any pt would mean infinite probability of finding the particle at that point which is not possible.
2. The wave function should be single valued at all points: It must have one and only one value at a particular point. This restriction arises because the probability at any given point must be unambiguous.
3. The wave function and its derivative must be continuous at all points in the space specified for the system: They must not change abruptly at any point for a slight change in the coordinates. The continuity of $d\psi/dx$ means there must not be any inflexion in ψ v/s x curve at any point. Expressed mathematically, $\psi(x)$ is continuous at the point $x=a$, if $\lim_{h \rightarrow 0} \psi(a+h) = \lim_{h \rightarrow 0} \psi(a-h)$, where h is the infinitesimal change in the value of x , at $x=a$.

4. The probability of finding the e^- overall the space from $-\infty$ to $+\infty$ must be 1, i.e., the ψ should be normalised.

$$\int_{-\infty}^{+\infty} \psi^2 d\tau = 1, \text{ where } d\tau = dx \cdot dy \cdot dz.$$

Several wave fn called $\psi_1, \psi_2, \psi_3 \dots$ etc will satisfy this condⁿ to the wave eqⁿ and each of these has corresponding energy E_1, E_2, E_3 etc.

$$\hat{H}\psi_1 = E_1\psi_1, \quad \hat{H}\psi_2 = E_2\psi_2 \text{ etc.}$$

This wave fn ψ_1, ψ_2, ψ_3 etc are known as orbitals.

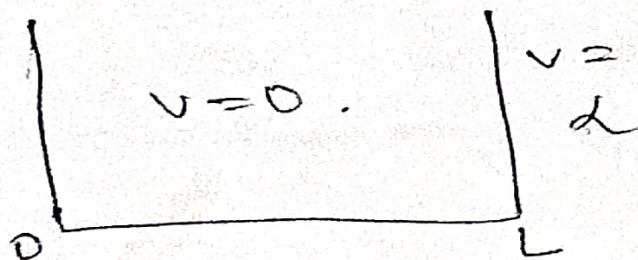
Interpretation of the wave function ψ

In the Schrodinger eqⁿ, the functⁿ ψ is used as a quantity analogous to amplitude in a classical wave. But, ψ is not a physically observable quantity although it can be used to determine all the physical quantities of the system through certain methods. These ~~f(x)~~ function, ψ is called a wave functⁿ. A physical intⁿ is given to ψ^2 (if ψ is real) or $\psi^* \psi$ (if ψ is complex and ψ^* is its conjugate) rather than ψ itself. The product functⁿ $\psi^* \psi$ is always a real quantity (let $\psi = Ae^{ix}$ and $\psi^* = Ae^{-ix}$ then $\psi^* \psi = Ae^{-ix} \cdot Ae^{ix} = |A|^2$). The conventional intⁿ that the ψ^2 at a point of classical wave represents energy density at that point is not acceptable because, energy of a particle is a discontd. functⁿ while ψ must be a continuous functⁿ. For an EM wave, Einstein intⁿ. ψ^2 at a point as probability density i.e. probability/unit space of finding the particle (e^-) at that point. A similar intⁿ was given by Max Born to ψ^2 for a particle wave. If a particle is moving in 1D, ψ^2 or $\psi^* \psi$ represents the probability of finding it within unit distance. Then, in an infinite ~~total~~ interval dx , around a point, the probability is $\psi^2 dx$ or $\psi^* \psi dx$. $\psi = \psi(x)$. In 3D, the probability is $\psi^2 dx dy dz$ or $\psi^* \psi dx dy dz$ where $\psi = \psi(x, y, z)$ and it refers to the probability that x, y, z coordinates of the particle lie within x and $x+dx$, y and $y+dy$ and z and $z+dz$ resp.^y. For a system of n particles in 3D, it will have its own ~~the~~ set of 3 coordinates $\rightarrow$ a total of $3n$ coordinates, $(x_1, y_1, z_1, \dots, x_n, y_n, z_n)$. Then, the prob. that the particle has coordinate (x, y, z) is given as $\psi^2 dx dy dz$; $dx = \text{vol}^m$ element of space and is given the symbol $d\tau$, for an e^- wave, another intⁿ of ψ^2 and $\psi^* \psi$ is given in terms e^- density i.e. e^- charge/unit space. This arises from the concept that e^- being a wave may be supposed to behave like a cloud of $-ve$ charge with non-uniform charge distribution. * (Consider the dual nature of EM radⁿ ... from Book Puri Sharma Kohli Pg-22)

① Particle in a box (translational motion of quantum mechanical / microscopic particle)

let us consider a free particle is confined to move in a 1D box, of length 'L', ($0 \leq x < L$) such that

$$\left\{ \begin{array}{ll} V = 0 & 0 < x < L \text{ (inside)} \\ V = \infty & x \leq 0 \text{ (outside)} \\ & x \geq L \end{array} \right\} .$$



Inside the box, $V=0$ because particle is free; i.e., no force acting on it.
 $F=0$

classically, $F = - \frac{dv}{dx}$

$$dv = 0$$

$$\int dv = 0$$

$$\therefore v = 0$$

$$\text{and } \frac{dv}{dx} = 0, \therefore v = \text{const}$$

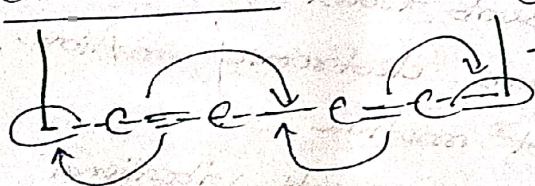
$v = \alpha$ outside ??

→ To avoid the Tunnelling.

Tunnelling → Quantum Mechanical phenomenon.

↓
Tendency of a Quantum mechanical particle to found in classically forbidden region is known as Tunnelling.

Particle in box → eg → V.B-butadiene



→ behaviour like particle in Box.

* Schrodinger eqⁿ in 1D box

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0$$

Inside box, $V = 0$

$$\therefore \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - 0) \psi = 0$$

$$\Rightarrow \frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2} \psi = 0 \quad \text{--- (1)}$$

let

$$\boxed{\frac{2mE}{\hbar^2} = k^2} \quad \text{--- (2)}$$

be comes,

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0.$$

above solution of the eqn are -

$$e^{ikx} + e^{-ikx}$$

$$\psi = C e^{ikx} + D e^{-ikx}$$

we know,

$$e^{i\theta} = \cos\theta + i\sin\theta$$

$$e^{ikx} = \cos kx + i\sin kx$$

$$e^{-ikx} = \cos kx - i\sin kx$$

now, $\psi = (C e^{ikx} + D e^{-ikx})$

$$= C [\cos kx + i\sin kx] + D [\cos kx - i\sin kx]$$

$$= (C+D) \cos kx + \sin kx [iC - iD]$$

$$= B \cos kx + A \sin kx$$

$$\psi = A \sin kx + B \cos kx \quad \text{--- (3)}$$

A and B are const, determined by boundary conditions. $\rightarrow \psi$ must be zero at boundary

at $x=0$, (1st Boundary).

ψ must be zero

$$0 = A \sin^0 k(0) + B \cos k(0)$$

$$0 = B(1)$$

$$\Rightarrow B = 0 \quad \text{--- (4)}$$

The soln at having B, is not acceptable, due to boundary condn.

Using $B=0$ in (3) we get

$$\boxed{\psi = A \sin kx} \rightarrow (5)$$

$x = L, \psi = 0$ (2nd Boundary condⁿ)

$$A \sin kL = 0$$

$A \neq 0$, if $A = 0$, then $\psi = 0$ (not possible)

$$\Rightarrow \sin kL = 0$$

$$\Rightarrow \sin kL = \sin n\pi \quad [n = 1, 2, 3, \dots]$$

$$kL = n\pi$$

$$\Rightarrow \boxed{k = \frac{n\pi}{L}} \quad (6) \quad n = 1, 2, 3, \dots$$

$n = \text{translational Quantum no.}$

using (6) in (5),

$$\boxed{\psi = A \sin \frac{n\pi}{L} x} \quad n = 1, 2, 3, \dots$$

On normalization,

$$\boxed{A = \sqrt{\frac{2}{L}}}$$

$$\Rightarrow \boxed{\psi = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x} \quad n = 1, 2, 3, \dots$$

Energy :-

$$k = \frac{n\pi}{L}$$
$$k^2 = \frac{n^2 \pi^2}{L^2}$$

$$\text{also, } k^2 = \frac{2mE}{\hbar^2}$$

$$\therefore \frac{n^2 \pi^2}{L^2} = \frac{2mE}{\hbar^2}$$

$$\Rightarrow \boxed{E = \frac{n^2 \pi^2 \hbar^2}{2mL^2} = \frac{n^2 \hbar^2}{8mL^2}} \quad n = 1, 2, 3, \dots$$

$$\frac{n^2}{0.1^2} = 1 \text{ eV}$$