Thomson model of atom

Thomson's model of an atom. In 1898, J.J. Thomson proposed that an atom is a sphere of positively charged matter with electrons embedded in it. The positive charge is uniformly distributed over the entire atom. The arrangement of electrons inside the atom is similar to that of the *seeds in a watermelon or the plums in a pudding*. That is why Thomson's atomic model is also known as *plum pudding model*. The electrons are arranged in such a manner that their mutual repulsions are balanced by their attractions with the positively charged matter. Thus the atom as a whole is stable and neutral.
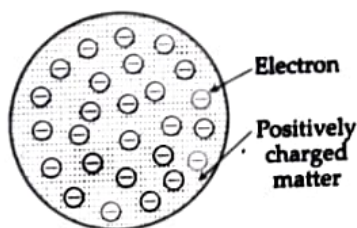

Fig. 11.1 **Plum pudding model of an atom.**

Failure of Thomson's model. Thomson model remained popular till about 1911 and was discarded later on due to the following drawbacks :

1. It could not explain the origin of several spectral series in the case of hydrogen and other atoms.
2. It failed to explain the large angle scattering of α-particles in Rutherford's experiment.

Rutherford Experiment

An α-particle is a helium ion, i.e., a helium atom from which both the electrons have been removed. It has charge equal to + 2e and its mass is nearly four times the mass of a proton.

Experimental arrangement. A schematic arrangement of the Geiger-Marsden experiment is shown in Fig. 11.2. A radioactive source of α-particles like $^{214}_{83}Bi$ is enclosed in thick lead block, provided with a narrow opening. The α-particles from this source are collimated into a narrow beam through a narrow slit. The beam is allowed to fall on a thin gold foil of thickness 2.1×10^{-7} m. The α-particles scattered in different directions are observed with the help of a rotatable detector which consists of a zinc sulphide screen and a microscope. Whenever an α-particle strikes the screen, it produces a tiny flash, which is viewed through the microscope. In this way, the number of α-particles scattered at different angles can be counted. The whole apparatus is enclosed in an evacuated chamber to avoid scattering of α-particles by air molecules.
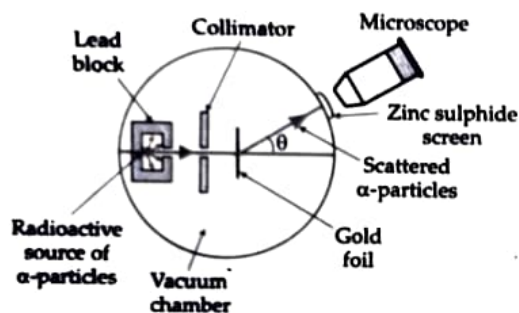

Fig. 11.2 **α-particle scattering experiment.**

Observations. As shown in Fig. 11.3, a graph is drawn between the scattering angle θ and the number N(θ) of the α-particles scattered at an angle θ, for a very large number of α-particles.
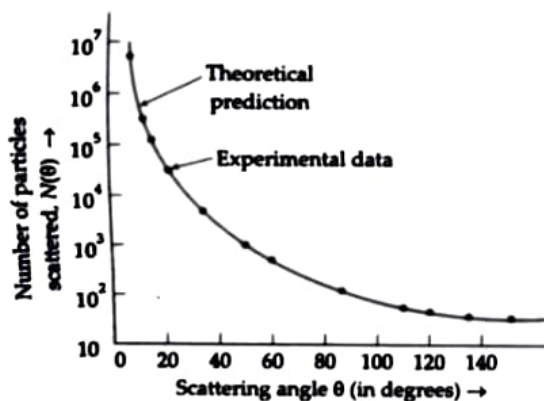

Fig. 11.3 **Graph of the total number of α-particles scattered at different angles θ.**

The above graph reveals the following facts :

1. Most of the α-particles pass straight through the gold foil or suffer only small deflections.

①

2. A few α-particles, about 1 in 8,000, get deflected through 90° or more.

3. Occasionally, an α-particle gets rebounded from the gold foil, suffering a deflection of nearly 180°.

Significance of the result. Rutherford concluded the following important facts about an atom :

1. As most of the α-particles pass straight through the foil, so most of the space within atoms must be empty.

2. To explain large angle scattering of α-particles, Rutherford suggested that all the positive charge and the mass of the atom is concentrated in a very small region, called the nucleus of the atom.

3. The nucleus is surrounded by a cloud of electrons whose total negative charge is equal to the total positive charge on the nucleus so that the atom as a whole is electrically neutral.

The scattering of the α-particles is due to the Coulombic repulsion between the positively charged α-particles and the nuclei. An α-particle like 1 or 1′, passing through the atom at large distance from the nucleus, experiences small repulsion and passes almost undeflected. But the α-particles like (2,2′), (3,3′) which pass closer to the nucleus, experience large repulsive forces and hence scatter through large angles. Very rarely, an α-particle like 4 travels head-on towards the nucleus. The strong repulsive force slows down the α-particle, which is finally stopped and then repelled back along its original path.
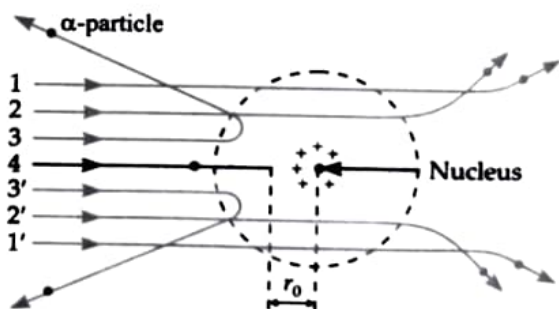

Fig. 11.4 Scattering of α-particles on the Rutherford model.

Distance of closest approach

Distance of closest approach : Estimation of nuclear size. As shown in Fig. 11.5, suppose an α-particle of mass m and initial velocity v moves directly towards the centre of the nucleus of an atom. As it approaches

the positive nucleus, it experiences Coulombic repulsion and its kinetic energy gets progressively converted into electrical energy. At a certain distance r_0 from the nucleus, the α-particle stops for a moment and then begins to retrace its path, i.e., it is scattered through an angle of 180°. The distance r_0 is called the distance of closest approach. At this distance r_0, the entire initial kinetic energy of the α-particle gets converted into electrostatic potential energy.
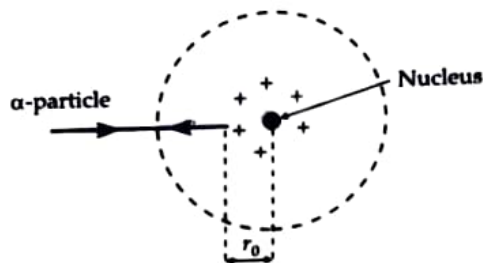

Fig. 11.5 Distance of closest approach.

Now, charge on an α-particle, $q_1 = +2e$

Charge on a scattering nucleus, $q_2 = +Ze$

where Z is the atomic number of foil atoms.

Initial kinetic energy of α-particle, $K_\alpha = \frac{1}{2}mv^2$

Electrostatic P.E. of α-particle and nucleus at distance r_0,

$$U = k \cdot \frac{q_1 q_2}{r_0} = k \cdot \frac{2e \cdot Ze}{r_0}$$

By conservation of energy, $K_\alpha = U$

or $\qquad K_\alpha = \frac{1}{2}mv^2 = k \cdot \frac{2Ze^2}{r_0}$

∴ $\qquad r_0 = \frac{2kZe^2}{K_\alpha} = \frac{4k\,Ze^2}{mv^2}$

where $k = \frac{1}{4\pi\varepsilon_0} = 9 \times 10^9 \ Nm^2 C^{-2}$.

Clearly, the radius of the nucleus must be smaller than r_0.

In one of the Rutherford's experiments, α-particles of energy 5.5 MeV were used.

∴ $\qquad K_\alpha = 5.5 \ MeV = 5.5 \times 1.6 \times 10^{-13} J$

Atomic number of gold, Z = 79

∴ $\qquad r_0 = \frac{2k\,Ze^2}{K_\alpha}$

$$= \frac{2 \times 9 \times 10^9 \times 79 \times (1.6 \times 10^{-19})^2}{5.5 \times 1.6 \times 10^{-13}}$$

$$= 4.13 \times 10^{-14} m = 41.3 \ fm$$

radius of a nucleus is of the order of a fermi, where 1 fermi (fm) = 10^{-15} m.

Impact parameter

Impact parameter. The scattering of an α-particle from a nucleus depends on its distance of closest approach to the nucleus or on an equivalent length, called the **impact parameter** 'b' as shown in Fig. 11.6.
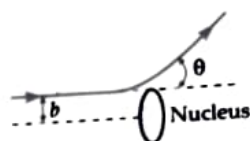
Fig. 11.6 Impact parameter b and scattering angle θ.

The impact parameter is defined as the perpendicular distance of the velocity vector of the α-particle from the centre of the nucleus, when it is far away from the atom.

From experiments, one can notice the following points :

1. For large impact parameters, the repulsive force experienced by the α-particle is weak

2. For small impact parameter, the repulsive force is large and so the α-particle is scattered through large angle.

3. For a head-on collision, when the α-particle just aims at the centre of the nucleus, *the impact parameter b = 0, scattering angle θ = 180°, i.e.,* the α-particle is reversed back along its original path.

Thus the shape of the trajectory of the scattered α-particles depends on the impact parameter and the nature of the potential field.

Rutherford deduced the following relationship between the impact parameter b and the scattering angle θ :

$$b = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2 \cot\frac{\theta}{2}}{K}$$

or

$$b = \frac{1}{4\pi\varepsilon_0}\cdot\frac{Ze^2 \cot\frac{\theta}{2}}{\frac{1}{2}mv^2}$$

The scattering experiments provide a method for investigating the nature of the forces involved.

Theory of Rutherford model

1. *An atom consists of a small and massive central core in which the entire positive charge and almost the whole mass of the atom are concentrated. This core is called the nucleus.*

2. *The size of the nucleus ($\approx 10^{-15}$ m) is very small as compared to the size of the atom ($\approx 10^{-10}$ m).*

3. *The nucleus is surrounded by a suitable number of electrons so that their total negative charge is equal to the total positive charge on the nucleus and the atom as a whole is electrically neutral.*

4. *The electrons revolve around the nucleus in various orbits just as planets revolve around the sun. The centripetal force required for their revolution is provided by the electrostatic attraction between the electrons and the nucleus.*

Limitations of Rutherford's atomic model :

1. According to *electromagnetic theory*, an accelerated charged particle must radiate electromagnetic energy. An electron revolving around the nucleus is under continuous acceleration towards the centre. It should continuously lose energy and move in orbits of gradually decreasing radii. The electron should follow a spiral path and finally it should collapse into the nucleus. Thus the *Rutherford's model cannot explain the stability of an atom.*

2. As the electrons spiral inwards, their angular velocities and frequencies would change continuously, and so the frequency of emitted light will also change. They would emit a continuous spectrum instead of the actually observed line spectrum.
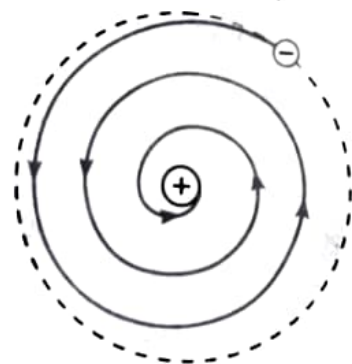
Fig. 11.7 Spiral path of an accelerated electron.

Bohr's Quantisation Condition

Bohr's quantisation condition of angular momentum. Consider the motion of an electron in a circular orbit of radius r around the nucleus of the atom. According to de Broglie hypothesis, this electron is also associated with wave character. Hence a circular orbit can be taken to be a stationary energy state only if it contains an integral number of de-Broglie wavelengths, *i.e.,* we must have

$$2\pi r = n\lambda$$

(a)

(b)

③
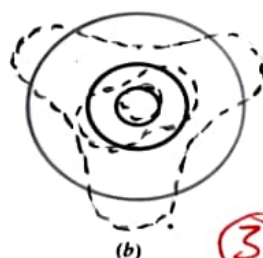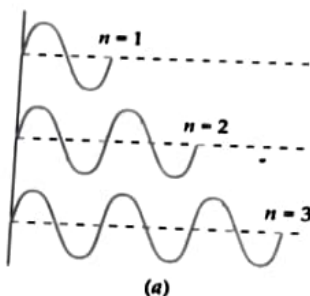
But de Broglie wavelength, $\lambda = \dfrac{h}{mv}$

$\therefore \qquad 2\pi r = \dfrac{nh}{mv}$

The angular momentum L of the electron must be

$$L = mvr = \dfrac{nh}{2\pi}, \qquad n = 1, 2, 3 .....$$

This is the famous *Bohr's quantisation condition for angular momentum* (Thus only those circular orbits can be the allowed stationary states of an electron in which its angular momentum is an integral multiple of $h/2\pi$.)

Bohr's Postulates

1. Nuclear concept. *An atom consists of a small and massive central core, called nucleus around which planetary electrons revolve. The centripetal force required for their rotation is provided by the electrostatic attraction between the electrons and the nucleus.*

2. Quantum condition. *Of all the possible circular orbits allowed by the classical theory, the electrons are permitted to circulate only in those orbits in which the angular momentum of an electron is an integral multiple of $\dfrac{h}{2\pi}$; h being Planck's constant.* Therefore, for any permitted orbit,

$$L = mvr = \dfrac{nh}{2\pi}, \qquad n = 1, 2, 3 ......$$

where L, m and v are the angular momentum, mass and speed of the electron, r is the radius of the permitted orbit and n is positive integer called *principal quantum number.* The above equation is *Bohr's famous quantum condition.*

3. Stationary orbits. *While revolving in the permissible orbits, an electron does not radiate energy. These non-radiating orbits are called stationary orbits.*

4. Frequency condition. *An atom can emit or absorb radiation in the form of discrete energy photons only when an electron jumps from a higher to a lower orbit or from a lower to a higher orbit, respectively. If E_1 and E_2 are the energies associated with these permitted orbits, then the frequency v of the emitted or absorbed radiation is given by*

$$hv = E_2 - E_1$$

This is Bohr's famous frequency condition.

Bohr's theory of hydrogen atom

Ms

Bohr's Theory of hydrogen atom : Radii of permitted orbits. According to Bohr's theory, a hydrogen atom consists of a nucleus with a positive charge Ze, and a single electron of charge $-e$, which revolves around it in a circular orbit of radius r. Here Z is the atomic number and for hydrogen $Z = 1$. The electrostatic force of attraction between the nucleus and the electron is

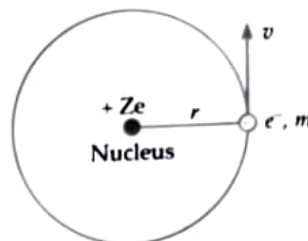$$F = \dfrac{k \, Ze.e}{r^2} = \dfrac{k \, Ze^2}{r^2}$$

Fig. 11.9 Bohr's model of hydrogen atom.

To keep the electron in its orbit, the centripetal force on the electron must be equal to the electrostatic attraction. Therefore,

$$\dfrac{mv^2}{r} = \dfrac{k \, Ze^2}{r^2}$$

or $\qquad mv^2 = \dfrac{k \, Ze^2}{r}$ $\qquad\qquad ...(1)$

or $\qquad r = \dfrac{k \, Ze^2}{mv^2}$ $\qquad\qquad ...(2)$

where m is the mass of the electron and v, its speed in an orbit of radius r.

Bohr's quantisation condition for angular momentum is

$$L = mvr = \dfrac{nh}{2\pi}$$

or $\qquad r = \dfrac{nh}{2\pi mv}$ $\qquad\qquad ...(3)$

From equations (2) and (3), we get

$$\dfrac{k \, Ze^2}{mv^2} = \dfrac{nh}{2\pi mv}$$

or $\qquad v = \dfrac{2\pi k \, Ze^2}{nh}$

Substituting this value of v in equation (3), we get

$$r = \dfrac{nh}{2\pi m} \cdot \dfrac{nh}{2\pi k \, Ze^2}$$

or $\qquad r = \dfrac{n^2 h^2}{4\pi^2 \, mk \, Ze^2}$ $\qquad\qquad ...(5)$

Clearly, the radii of the permitted orbits are proportional to n^2 and increase in the ratio of $1 : 4 : 9 : 16....$ The parameter n is called the *principle quantum number.*

The radius of the innermost orbit of the hydrogen atom, called **Bohr's radius** can be determined by putting $Z = 1$ and $n = 1$ in equation (5) and it is denoted by r_0.

$$\therefore \quad r_0 = \frac{h^2}{4\pi^2 \, m \, ke^2}$$

$$= \frac{(6.63 \times 10^{-34})^2}{4\pi^2 \times 9.11 \times 10^{-31} \times 9 \times 10^9 \times (1.6 \times 10^{-19})^2} \text{ m}$$

$$= 5.29 \times 10^{-11} \text{ m} \approx 0.53 \text{ Å}.$$

Speed of electron. From equation (4), the orbital speed of electron is

$$v = \frac{2\pi k \, Ze^2}{nh}$$

For hydrogen, $Z = 1$, therefore,

$$v = \frac{2\pi ke^2}{nh} = \left(\frac{2\pi ke^2}{ch}\right)\frac{c}{n}$$

or

$$v = \alpha . \frac{c}{n}$$

The quantity $\alpha = \frac{2\pi ke^2}{ch}$, is a dimensionless constant and is called *fine structure constant.* Its value is

$$\alpha = \frac{2\pi \times 9 \times 10^9 \times (1.6 \times 10^{-19})^2}{3 \times 10^8 \times 6.63 \times 10^{-34}} = \frac{1}{137}$$

$$\therefore \quad v = \frac{1}{137} . \frac{c}{n}$$

For first orbit $(n = 1)$, $\quad v = \frac{c}{137}$

Thus the speed of the electron in the innermost orbit is $1/137$ of the speed of light in vacuum, while the speed in the outer orbits varies inversely with n.

Energy of the electron. It includes the electron's kinetic energy and the electrostatic potential energy of the two charges.

Kinetic energy of the electron in nth orbit is

$$\text{K.E.} = \frac{1}{2} mv^2 = \frac{k \, Ze^2}{2r} \text{ [Using equation (1)]}$$

Potential energy of the electron in nth orbit is

$$\text{P.E.} = k \frac{q_1 q_2}{r} = \frac{k \, Ze.(-e)}{r} = -\frac{k \, Ze^2}{r}$$

Hence total energy of the electron in nth orbit is

$$E_n = \text{K.E.} + \text{P.E.}$$

$$= \frac{k \, Ze^2}{2r} - \frac{k \, Ze^2}{r} = -\frac{k \, Ze^2}{2r}$$

$$= -\frac{k \, Ze^2}{2} . \frac{4\pi^2 \, mk \, Ze^2}{n^2 h^2}$$

[Using equation (5)]

or

$$E_n = -\frac{2\pi^2 \, mk^2 \, Z^2 e^4}{n^2 h^2} \qquad \text{...(6)}$$

The negative value of the total energy indicates that the electron is bound to the nucleus by means of electrostatic attraction and some work is required to be done to pull it away from the nucleus.

Spectral series of hydrogen atom

Spectral series of hydrogen atom. From Bohr's theory, the energy of an electron in the nth orbit of hydrogen atom is given by

$$E_n = -\frac{2\pi^2 \, mk^2 \, Z^2 \, e^4}{h^2} . \frac{1}{n^2}$$

According to *Bohr's frequency condition,* whenever an electron makes a transition from a higher energy level n_2 to a lower energy level n_1, the difference of
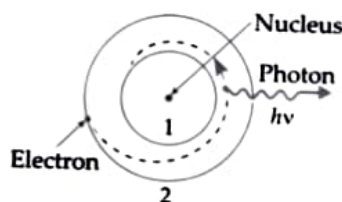

Fig. 11.10 Emission of a spectral line by a hydrogen atom.

energy appears in the form of a photon. The frequency v of the emitted photon is given by

$$hv = E_{n_2} - E_{n_1}$$

or

$$hv = \frac{2\pi^2 \, mk^2 e^4}{h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

or

$$v = \frac{2\pi^2 \, mk^2 e^4}{h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

As $c = v\lambda$, therefore **wave number** $\bar{v}$, *which is the reciprocal of wavelength* λ, is given by

$$\bar{v} = \frac{1}{\lambda} = \frac{v}{c} = \frac{2\pi^2 \, mk^2 e^4}{ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

or
$$\bar{v} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

where $R = \dfrac{2\pi^2 mk^2 e^4}{ch^3}$, is the *Rydberg constant* and its value is 1.0973×10^7 m^{-1}. The above equation is the **Rydberg formula** for the spectrum of hydrogen atom.
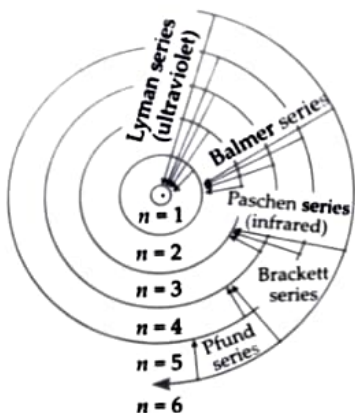

Fig. 11.11 Spectral series of hydrogen atom.

As shown in Fig. 11.11, the origin of the various series in the hydrogen spectrum can be explained as follows :

(*i*) **Lyman series.** If an electron jumps from any higher energy level $n_2 = 2, 3, 4......$ to a lower energy level $n_1 = 1$, we get a set of spectral lines called *Lyman series* which belong to the *ultraviolet region* of the electromagnetic spectrum. This series is given by

$$\bar{v} = \frac{1}{\lambda} = R\left[\frac{1}{1^2} - \frac{1}{n_2^2}\right], \quad n_2 = 2, 3, 4......$$

(*ii*) **Balmer series.** The spectral series corresponding to the transitions $n_2 = 3, 4, 5......$ to $n_1 = 2$, lies in the *visible region* and is called *Balmer series*. For this series,

$$\bar{v} = \frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{n_2^2}\right], \quad n_2 = 3, 4, 5......$$

(*iii*) **Paschen series.** If $n_2 = 4, 5, 6......$ and $n_1 = 3$, we get a spectral series in the *infrared region* which is called *Paschen series*.

$$\bar{v} = \frac{1}{\lambda} = R\left[\frac{1}{3^2} - \frac{1}{n_2^2}\right], \quad n_2 = 4, 5, 6......$$

(*iv*) **Brackett series.** If $n_2 = 5, 6, 7......$ and $n_1 = 4$, we get a spectral series in the *infrared region* which is called *Brackett series*.

$$\bar{v} = \frac{1}{\lambda} = R\left[\frac{1}{4^2} - \frac{1}{n_2^2}\right], \quad n_2 = 5, 6, 7......$$

(*v*) **Pfund series.** If $n_2 = 6, 7, 8......$ and $n_1 = 5$, we get a spectral series in the *infrared region* which is called *Pfund series*.

$$\bar{v} = \frac{1}{\lambda} = R\left[\frac{1}{5^2} - \frac{1}{n_2^2}\right], \quad n_2 = 6, 7, 8......$$

Energy diagram for hydrogen

Energy level diagram. *It is a diagram in which the energies of the different stationary states of an atom are represented by parallel horizontal lines, drawn according to some suitable energy scale.* Such a diagram illustrates more clearly the known facts about the stationary states and the emission or absorption of various spectral lines.

Energy levels of hydrogen. From Bohr's theory, the total energy of an electron in nth orbit is given by

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

For hydrogen $Z = 1$, therefore,

$$E_n = -\frac{2\pi^2 mk^2 e^4}{h^2} \cdot \frac{1}{n^2}$$

Energy of the electron in the first orbit $(n = 1)$ is given by

$$E_1 = -\frac{2 \times (3.14)^2 \times 9.11 \times 10^{-31} \times (9 \times 10^9)^2 \times (1.6 \times 10^{-19})^4}{(6.63 \times 10^{-34})^2} \cdot \frac{1}{1^2}$$

$$= -21.76 \times 10^{-19} \text{ J} = -\frac{21.76 \times 10^{-19}}{1.6 \times 10^{-19}} \text{ eV}$$

$$= -13.6 \text{ eV} \qquad [\because 1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}]$$

Hence we can write,

$$E_n = \frac{E_1}{n^2} = -\frac{13.6}{n^2} \text{ eV}$$

Setting $n = 2, 3, 4$, etc., we get the energies for the higher orbits as follows :

$$E_2 = \frac{-13.6}{2^2} = -3.4 \text{ eV}$$

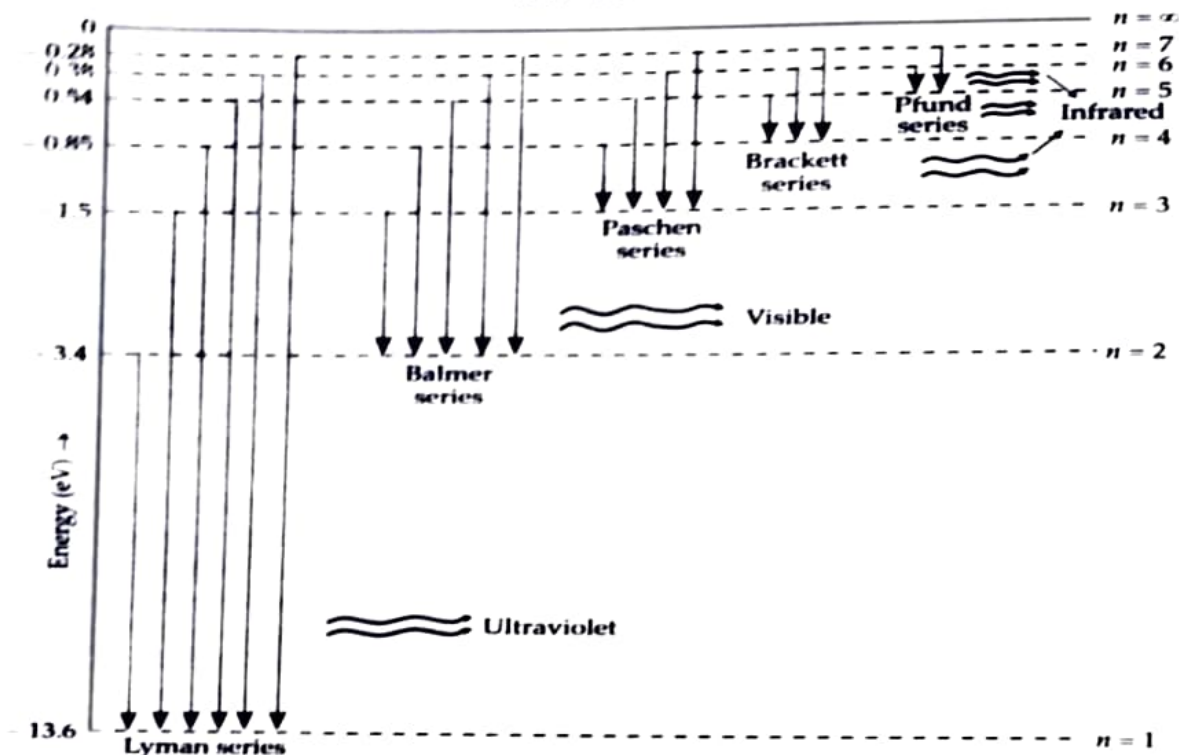$$E_3 = \frac{-13.6}{3^2} = -1.51 \text{ eV}$$

Fig. 11.12 Energy level diagram of hydrogen atom and its various spectral series.

$$E_4 = \frac{-13.6}{4^2} = -0.85 \text{ eV}$$

$$E_5 = \frac{-13.6}{5^2} = -0.54 \text{ eV}$$

$$E_6 = \frac{-13.6}{6^2} = -0.38 \text{ eV}$$

Clearly, *an electron can have only certain definite values of energy while revolving in different orbits. This is called* **energy quantisation**.

The energy state corresponding to $n = 1$, has the lowest energy equal to –13.6 eV. *This state or orbit is called the* **ground** *or* **normal state** of the atom. Normally the electron in the hydrogen atom remains in the ground state. When the hydrogen atom receives energy from outside by processes such as electron collisions, the electron may make transition to some higher energy state like E_2, E_3, E_4, etc. which are called the **excited states**.

Limitations

Limitations of Bohr's theory. Although Bohr's theory could successfully explain the spectrum of hydrogen, yet it had the following shortcomings :

1. This theory is applicable only to hydrogen-like single electron atoms and fails in the case of atoms with two or more electrons.

2. In the spectrum of hydrogen, certain spectral lines are not single lines but a group of closed lines with slightly different frequencies. Bohr's theory could not explain these fine features of the hydrogen spectrum.

3. It does not explain why only circular orbits should be chosen when elliptical orbits are also possible.

4. As electrons exhibit wave properties also, so orbits of electrons cannot be exactly defined as in Bohr's theory.

5. Bohr's theory does not tell anything about the relative intensities of the various spectral lines. Bohr's theory predicts only the frequencies of these lines.

6. It does not explain the further splitting of spectral lines in a magnetic field (**Zeeman effect**) or in an electric field (**Stark effect**).

⑦

Excitation energy. *The excitation energy of an atom is defined as the energy required by its electron to jump from the ground state to any one of the excited states.*

First excitation energy of hydrogen

$$= E_2 - E_1 = -3.4 - (-13.6) = 10.2 \text{ eV}$$

Second excitation energy of hydrogen

$$= E_3 - E_1 = -1.51 - (-13.6) = 12.09 \text{ eV}.$$

Ionisation Energy. *It is defined as the energy required to knock an electron completely out of the atom, i.e., the energy required to take an electron from its ground state to the outermost orbit ($n = \infty$). After the removal of the electron, the atom is left with positive charge and it is said to ionised.*

Ionisation energy of hydrogen

$$= E_\infty - E_1 = 0 - (-13.6) = 13.6 \text{ eV}.$$

Excitation potential. *It is that accelerating potential which gives to a bombarding electron, sufficient energy to excite the target atom by raising one of its electrons from an inner to an outer orbit.*

First excitation potential of hydrogen

$$= -3.4 - (-13.6) = 10.2 \text{ V}$$

Second excitation potential of hydrogen

$$= -1.51 - (-13.6) = 12.09 \text{ V}.$$