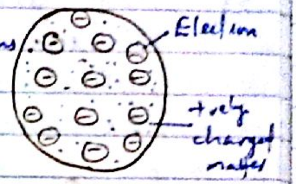
ATOMS.

Thomson's model of an atom

An atom consists of a sphere of +vely charged matter in which the -vely charged electrons are uniformly embedded like the plums in a pudding.

The mutual repulsion between electrons are balanced by their attractions with the +vely charged matter. Thus the atom as a whole is stable and neutral.

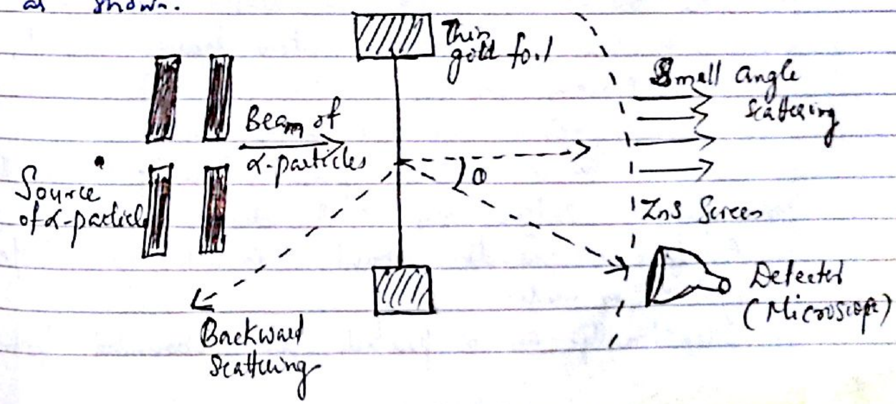


Failure of Thomson's model.

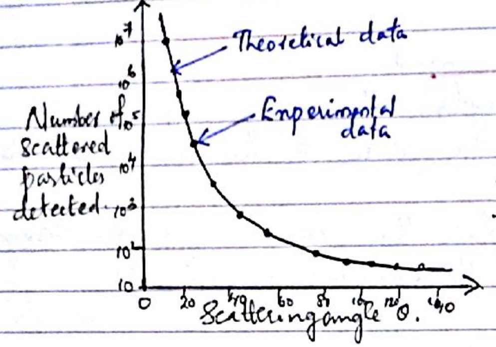
1. It could not explain the origin of several spectral series in the case of hydrogen and other atoms.
2. It failed to explain the large angle scattering of α- particles in Rutherford's experiment.

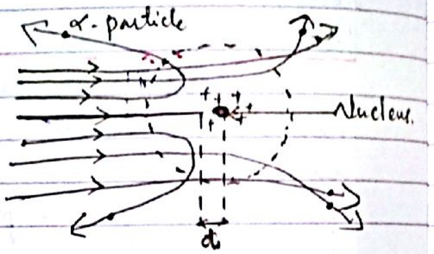
[Alpha - Particle Scattering Experiment]

At the suggestion of Ernst Rutherford, H Geiger and E. Marsden performed α- particle scattering experiment. The Schematic arrangement of this experiment is as shown.



A radioactive source of α-particle like $_{83}Bi^{214}$ 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.





A typical graph of the total no. of α-particles scattered at different angles, in a given time interval is as shown. The dots in this figure represent the data points and the solid curve is the theoretical prediction based on the assumption that the target atom has a small, dense, positively charged nucleus.

The graph reveals the following facts.

1. Most of the α-particles pass straight through the gold foil or suffer only small deflection.
2. A few α-particles, about 1 in 8000, get deflected through 90° or more.
3. Occasionally an α-particle gets rebounded from the gold foil, suffering a deflection of nearly 180°.

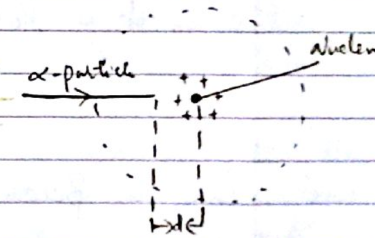
From these facts Rutherford concluded that

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-particle 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.

Distance of closest approach: Estimation of nuclear size.

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 experience Coulombic repulsion and its K.E gets progressively converted into electrical energy. At a certain 'd' from the nucleus the α-particle stops for a moment and then begins to retrace its path. The distance 'd' is called the distance of closest approach.



Initial K.E of α-particle =
$$K = \frac{1}{2} m v^2.$$

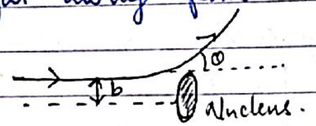
Electrostatic P.E of α-particle and nucleus at distance d

$$U = \frac{1}{4\pi\varepsilon_0} \frac{(2e)(Ze)}{d}.$$
$$= \frac{2Ze^2}{4\pi\varepsilon_0 d}$$

At the distance d, $K = U$.
$$K = \frac{2Ze^2}{4\pi\varepsilon_0 d}$$

$$\therefore d = \frac{2Ze^2}{4\pi\varepsilon_0 K}$$
$$= \frac{2Ze^2}{4\pi\varepsilon_0 \cdot \frac{1}{2}mv^2} = \frac{4Ze^2}{4\pi\varepsilon_0 mv^2}.$$
$$= \frac{Ze^2}{mv^2\pi\varepsilon_0}.$$

Impact Parameter :- It 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



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

where θ is the angle of scattering.

Rutherford's model of an atom.

On the basis of the α-particle scattering experiment, Rutherford proposed the following model of an atom.

1. An atom consists of a small and massive central core in which 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 is very small as compared to the size of atom.

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 planet 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.

Rutherford's model has two main difficulties in explaining the structure of atom.

1. It predicts that atoms are unstable because the accelerated electrons revolving around the nucleus must radiate energy and move spirally into the nucleus. This contradicts the stability of matter.

2. It cannot explain the characteristic line spectra of atoms of different elements.

Energy of an electron.

According to Rutherford model of the atom electrons are revolving around the nucleus. The electrostatic force of attraction F_e between the revolving electrons and the nucleus provides the requisite centripetal force F_c to keep them in their orbits.

ie $F_e = F_c$

$$\frac{1}{4\pi\epsilon_0}\frac{e^2}{r^2} = \frac{mv^2}{r}$$

$$\therefore r = \frac{e^2}{4\pi\epsilon_0 mv^2} \quad \text{and} \quad v^2 = \frac{e^2}{4\pi\epsilon_0 rm}$$

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

$$= \frac{e^2}{8\pi\epsilon_0 r}.$$

P.E 'U' of the electron $U = \frac{-1}{4\pi\epsilon_0}\frac{e^2}{r}$

The negative sign in U signifies that the electrostatic force is in the $-r$ direction.

Thus the total energy

$$E = K + U$$

$$= \frac{e^2}{8\pi\epsilon_0 r} + \frac{-e^2}{4\pi\epsilon_0 r}$$

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

The total energy of the electron is negative. This implies that the electron is bound to the nucleus. If 'E' were +ve an electron will not follow a closed orbit around the nucleus.

Bohr Postulates of Atom.

Bohr model also called Planetary model of the atom is based on the following postulates

(i) Nuclear Concept :- An atom consists of a small and massive core called nucleus around which planetary e's revolve. The centripetal force required for their rotation is provided by the electrostatic attraction between the electrons and nucleus.

(ii) Quantum Condition :- The electrons revolves around the nucleus only in those orbits for which the angular momentum is an integral multiple of $\frac{h}{2\pi}$ ie for any permitted orbit $L = \frac{nh}{2\pi}$ where $n = 1, 2, 3 \ldots$

(iii) Stationary Orbits :- While revolving in the permissible orbits, an electron does not radiate energy. The non-radiating orbits are called Stationary orbits.

(iv) 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. If E_i and E_f are the energy associated with these permitted orbits then $E_i - E_f = h\nu$

de-Broglie's Explanation of Bohr's II postulate. [Bohr 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 a stationary energy state only if it contain an integral number of de-Broglie wave lengths

ie $2\pi r = n\lambda$

But de-Broglie wavelength $\lambda = \frac{h}{mv}$.

$$\therefore 2\pi r = \frac{nh}{mv} \quad \therefore r = \frac{nh}{2\pi mv}$$

Angular momentum L of the electron must be

$$L = mvr$$
$$= \frac{\cancel{mv} \cdot nh}{2\pi \cancel{mv}}$$
$$L = \frac{nh}{2\pi} \quad \text{where } n = 1, 2, 3 \ldots$$

This is Bohr's quantisation condition of angular momentum.

<u>Bohr theory of hydrogen atom.</u>

According to Bohr theory a hydrogen atom consist of a nucleus with a positive charge e and a single electron of charge e which revolves around it in a circular orbit of radius r_n where r_n is the radius of n^{th} possible orbit.

Hence $F_e = F_c$

$$\frac{1}{4\pi\epsilon_0}\frac{e^2}{r_n^2} = \frac{mv_n^2}{r_n}$$

$$\therefore r_n = \frac{e^2}{4\pi\epsilon_0 m v_n^2} \quad \text{—— (1)}$$

According to Bohr quantisation condition for n^{th} orbit

$$L_n = mv_n r_n = \frac{nh}{2\pi}$$

$$\therefore r_n = \frac{nh}{2\pi m v_n} \quad \text{—— (2)}$$

from (1) and (2)

$$\frac{e^2}{4\pi\epsilon_0 m v_n^2} = \frac{nh}{2\pi m v_n}$$

$$\frac{e^2}{4\pi\epsilon_0 v_n} = \frac{nh}{2\pi}$$

$$\therefore v_n = \frac{1}{n}\frac{e^2}{4\pi\epsilon_0}\frac{1}{(h/2\pi)} \quad \text{—— (3)}$$

Sub: the value v_n in eqn (2)

$$r_n = \frac{nh}{2\pi m \cdot \frac{1}{n}\frac{e^2}{4\pi\epsilon_0}\frac{1}{(h/2\pi)}}$$

$$= \frac{n^2}{m}\left(\frac{h}{2\pi}\right)^2 \cdot \frac{4\pi\epsilon_0}{e^2} \quad \text{—— (3)}$$

The size of the inner most orbit $n=1$ can be obtained as

$$r_1 = \frac{h^2\epsilon_0}{\pi m e^2}$$

This is called the Bohr radius, represented by the symbol r_0

$$\therefore \quad r_0 = \frac{h^2 \varepsilon_0}{\pi m e^2} \quad \text{—— (4)}$$

Substituting the values of h, m, ε_0 and e we get

$$r_0 = \frac{6.6\times10^{-34} \times 8.854\times10^{-12}}{3.14 \times 9.1\times10^{-31} \times (1.6\times10^{-19})^2}$$

$$= 5.29 \times 10^{-11} m.$$

from equ (3) it can be seen that the radii of the orbit increase as n^2.

The total energy of the electron

$$E_n = \frac{-e^2}{8\pi\varepsilon_0 r_n}$$

$$= \frac{-e^2}{8\pi\varepsilon_0}\left(\frac{m}{n^2}\right)\left(\frac{2\pi}{h}\right)^2\left(\frac{e^2}{4\pi\varepsilon_0}\right)$$

$$= \frac{-me^4}{8n^2\varepsilon_0^2 h^2} \quad \text{—— (5)}$$

Substituting values we get

$$E_n = \frac{-2.18\times10^{-18}}{n^2} \; J.$$

$$1eV = 1.6\times10^{-19} J.$$

$$\therefore \quad E_n = \frac{-2.18\times10^{-18}}{n^2 \times 1.6\times10^{-19}}$$

$$= \frac{-13.6}{n^2} \; eV.$$

The -ve sign of the total energy of an $\bar{e}$ moving in an orbit means that the electron is bound with the nucleus.

Speed of electron in n^{th} Orbit of H-atom.

According to Bohr's theory of H-atom

$$F_e = F_c$$

$$\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} = \frac{mv^2}{r}$$

$$\text{or} \quad r = \frac{e^2}{4\pi\varepsilon_0 m v^2}$$

$$\text{But} \quad L = mvr = \frac{nh}{2\pi}$$

$$r = \frac{nh}{2\pi m v}.$$

$$\therefore \quad \frac{e^2}{4\pi\varepsilon_0 m v^2} = \frac{nh}{2\pi m v}$$

$$\text{or} \quad v = \frac{e^2}{4\pi\varepsilon_0}\frac{2\pi}{nh}.$$

$$v = \frac{e^2}{4\pi\varepsilon_0}\frac{2\pi}{ch}\cdot\frac{c}{n}$$

$$= \alpha \cdot \frac{c}{n}$$

Here α is fine structure constant $\alpha = \frac{1}{137}$

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

In the innermost orbit $n = 1$ $\therefore$ $v = \frac{c}{137}$. Thus speed of an e in the innermost orbit of H-atom is 1/137 times the speed of light in vacuum

Spectral Series of hydrogen atom.

Total energy of the electron in the n^{th} orbit

$$E_n = \frac{-me^4}{8\varepsilon_0^2 h^2 n^2}$$

According to Bohr postulate when an atom makes a transition from the higher energy state with quantum number n_i to the lower energy state with quantum number n_f $(n_f < n_i)$ then

$$E_{n_i} - E_{n_f} = h\nu$$

$$\frac{-me^4}{8\varepsilon_0^2 h^2 n_i^2} + \frac{me^4}{8\varepsilon_0^2 h^2 n_f^2} = h\nu$$

$$\frac{me^4}{8\varepsilon_0^2 h^2}\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right] = h\nu$$

or $$\nu = \frac{me^4}{8\varepsilon_0^2 h^3}\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$$

$$\frac{\nu}{c} = \frac{me^4}{8\varepsilon_0^2 h^3 c}\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$$

The term $\frac{\nu}{c} = \frac{1}{\lambda}$ called wave number $\bar{\nu}$

$$\therefore \frac{1}{\lambda} = \bar{\nu} = \frac{me^4}{8\varepsilon_0^2 h^3 c}\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$$

or $\bar{\nu} = R\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$ where R is a constant $R = \frac{me^4}{8\varepsilon_0^2 h^3 c}$ called Rydberg constant and its value is $1.0973 \times 10^7\ m^{-1}$.

The above equation is also called Balmer formula

i.e. $$\frac{1}{\lambda} = R\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$$

The origin of various series in the H-atom can be explained as follows

1. Lymann Series :-

If an electron jumps from any higher level $n_i = 2, 3, 4$ to a lower energy level $n_f = 1$, we get a set of spectral lines called Lymann series which belong to the U.V region of the EM spectrum

$$\frac{1}{\lambda} = R\left[\frac{1}{1^2} - \frac{1}{n_i^2}\right] \text{ where } n_i = 2, 3, 4 \ldots$$

2. Balmer Series

If an electron jumps from any higher level $n_i = 3, 4, 5$ to a lower energy level $n_f = 2$ we get a set of spectral lines called Balmer series. which belong to the visible region of the EM spectrum.

$$\frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{n_i^2}\right] \text{ where } n_i = 3, 4, 5 \ldots$$

3. Paschen Series.

If an electron jumps from any higher level $n_i = 4, 5, 6$ to a lower energy level $n_f = 3$, we get a spectral lines called Paschen series which belong to the IR region of the EM Spectrum.

$$\frac{1}{\lambda} = R\left[\frac{1}{3^2} - \frac{1}{n_i^2}\right] \quad \text{where } n_i = 4, 5, 6 \ldots$$

Brackett Series

If an electron jumps from any higher level $n_i = 5, 6, 7 \ldots$ to a lower energy level $n_f = 4$, we get a spectral lines called Brackett series which belong to the IR regions of the EM spectrum.

$$\frac{1}{\lambda} = R\left[\frac{1}{4^2} - \frac{1}{n_i^2}\right] \quad \text{where } n_i = 5, 6, 7 \ldots$$

Pfund Series.

If an electron jumps from any higher level $n_i = 6, 7, 8 \ldots$ to a lower energy level $n_f = 5$ we get a spectral lines called Pfund series which belong to the IR Regions of the EM Spectrum.

$$\frac{1}{\lambda} = R\left[\frac{1}{5^2} - \frac{1}{n_i^2}\right] \quad \text{where } n_i = 6, 7, 8 \ldots$$

Energy level diagram for H

We have

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

$$E_1 = \frac{-13.6}{1^2} = -13.6\ \text{eV}$$

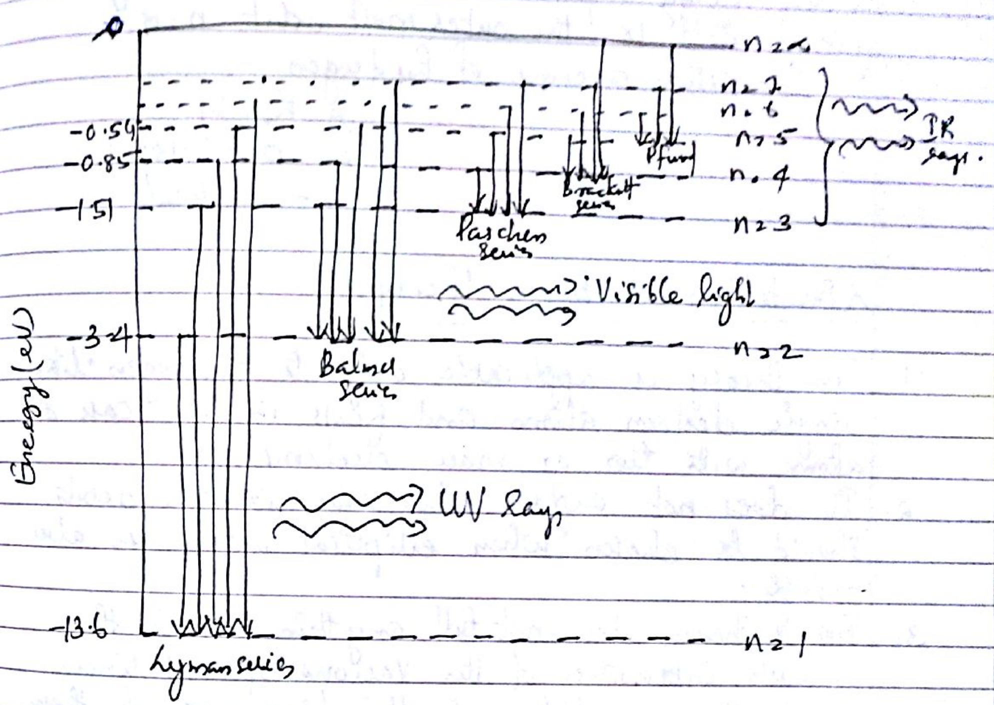
$$E_2 = \frac{-13.6}{2^2} = -3.4\ \text{eV}$$

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

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

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

$$E_\infty = \frac{-13.6}{\infty^2} = 0.$$



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

ie the energy required to take an electron from the ground state to the outer most orbit $n = \alpha$ ie

Ionisation energy of hydrogen

$$= E_\alpha - E_1$$
$$= 0 - (-13.6)$$
$$= \underline{13.6 eV}$$

Limitations of Bohr's theory.

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