

Thomson's Model Thomson in 1898, stated:

- Atom as a whole is neutral, i.e., positive and negative charge are equal.
- The positive charge and the whole mass is distributed uniformly like a cake and electrons are embedded like cherries in the cake. Therefore, this model is also called plum pudding model.
- It cannot explain α -particle scattering and spectrum of an atom.

In 1903, Leonard suggested that atom is made up of tiny particles carrying negative and positive charges. These are termed as electrons and protons. Leonard, however, could not explain why heating of metals does not eject positively charged particles.

Rutherford's Model

Rutherford conducted α -particle scattering experiment. On the basis of which he proposed a model of an atom.

- The whole positive charge and whole mass of the atom is concentrated in a very small region called nucleus. The size of the nucleus is $\sim 10^{-15}$ m or 1 fm.
- The electrons revolve around the nucleus in circular orbits. The size of an atom $\sim 10^{-10}$ m. There exists a large empty space around the nucleus.
- Atoms are electrically neutral

$$\text{Distance of closest approach } r = \frac{2Ze^2}{4\pi\epsilon_0(KE)}$$

$$\text{Impact parameter } b = \frac{Ze^2 \cot \frac{\theta}{2}}{4\pi\epsilon_0(KE)}$$

The number of particles scattered through an angle θ is given by

$$N(\theta) \propto \frac{Z^2}{\sin^4\left(\frac{\theta}{2}\right)(KE)^2}$$

This model failed to explain as to why the revolving electrons do not lose energy and ultimately fall into the nucleus following a spiral path, i.e., stability of atom could not be explained with this model.

Bohr's Model

When Bohr proposed his model hydrogen spectrum was known.

$$\text{Rydberg's empirical formula } \frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

was also known. By certain assumptions, called Bohr's postulates, he could manage to explain Hydrogen spectrum.

- electrons move around the nucleus in circular orbits.
- The orbits are stable called stationary orbits. They have special values of their radii such that angular momentum is quantized; i.e., $mvr = n\hbar$ where

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

- Energy is released when an electron makes a transition from higher to lower level as shown

in the Figure (a) and energy is absorbed when an electron jumps from lower to higher orbit as shown in the Figure (b)

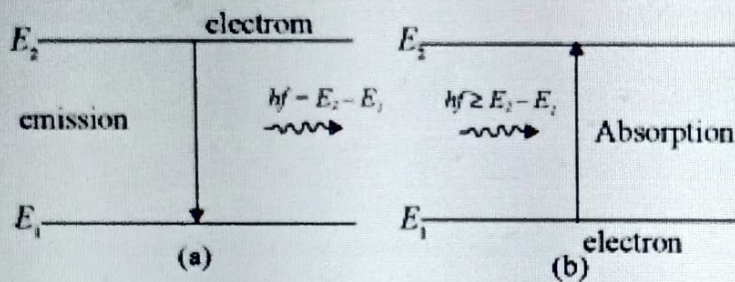


Fig. 18.1 Emission - Absorption of Radiation

The centripetal force is equal to the electrostatic force.

$$\text{Radius of } n\text{th orbit } r_n = \frac{n^2 \epsilon_0 h^2}{\pi m Z e^2}$$

$$\text{Bohr radius (1st orbit of H atom)} r_1 = \frac{\epsilon_0 h^2}{\pi m e^2} = 0.53 \text{ \AA}$$

$$r_n = n^2 r_1 \text{ for Hydrogen and}$$

$$r_n = \frac{n^2 r_1}{Z} \text{ for Hydrogen like atoms.}$$

$$\text{Orbital speed } v_n = \frac{e^2}{2\epsilon_0 n h} \text{ for Hydrogen}$$

$$\text{Energy of } n\text{th orbit } = E_n = KE_n + PE_n = \frac{mZ^2 e^4}{8\epsilon_0^2 h^2 n^2}$$

Note: If in place of m reduced mass be taken agreement is perfect. Reduced mass $m_r = \frac{m_p m_e}{m_p + m_e}$ where m_p and m_e are mass of proton and electron respectively. Bohr's analysis are within 0.1% of measured values.

Sommerfeld Model

The electrons revolve around the nucleus in elliptical orbits. The mass of the electron varies with velocity relativistically

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}$$

Total angular momentum of an electron is the resultant of orbital angular momentum and radial angular momentum. These two angular momentum are separately quantized.

De-Broglie Theory

A standing wave on a string transmits no energy. Therefore, think of an electron as a standing wave fitted in a circle in one of the Bohr orbits. Only those circular orbits are possible whose circumference is an integral multiple of de-Broglie wavelength associated with the electron, i.e., $2\pi r = n\lambda$ since $\lambda = \frac{h}{mv}$ thus, $mvr = \frac{nh}{2\pi}$ which matches with Bohr's quantization theory and suggests strongly that wave character of electrons is important in atomic structure.

Representation of waves associated with orbital electrons in an atom is illustrated in Fig. 18.2 for $n = 1$, $n = 2$, $n = 3$ and $n = 4$.

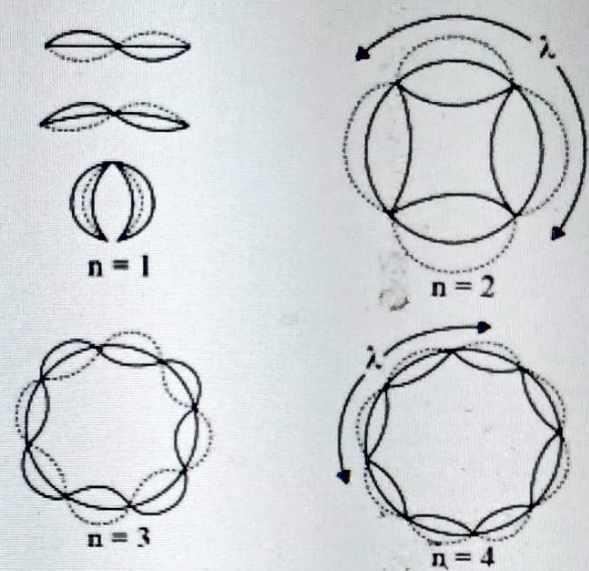


Fig. 18.2 de Broglie stationary waves in the orbit

$$\text{Velocity of electron in the } n\text{th orbit } v_n = \frac{2\pi Z e^2}{4\pi\epsilon_0 n h}$$

$$= \frac{c}{137}$$

$$= \frac{Z}{n} = 2.2 \times 10^6 \frac{Z}{n} \text{ ms}^{-1}$$

$$\alpha = \frac{2\pi Z e^2}{4\pi\epsilon_0 c h} = \frac{1}{137} \text{ is called fine structure constant.}$$

$$\text{Angular frequency of electron } \omega = \frac{8\pi^2 Z^2 e^4 m}{(4\pi\epsilon_0)^2 n^3 h^3}$$

$$= \frac{4.159 \times 10^6 Z^2}{n^3} \text{ rad s}^{-1}$$

Electric current due to electron motion in n th orbit

$$I_n = \frac{4\pi Z^2 e^5 m}{n^3 h^3 (4\pi\epsilon_0)^2} = \frac{1.06 Z^2}{n^3} \text{ mA}$$

Magnetic induction produced in the n th orbit

$$B_n = \frac{\mu_0 I_n}{2r_n} = \frac{8\pi^4 Z^3 e^7 m^2}{n^3 h^3 (4\pi\epsilon_0)^3} = \frac{1.258 Z^3}{n^3} \text{ Tesla}$$

Magnetic moment produced in the n th orbit

$$M_n = \frac{ehn}{2m} = \frac{ehn}{4\pi m} = 9.26 \times 10^{-24} n \text{ Am}^2$$

$$= n \text{ Bohr Magnetron.}$$

$$\text{KE of electron} = \frac{e^2 Z^2}{8\pi\epsilon_0 r_n} = \frac{13.6 Z^2}{n^2} \text{ eV}$$

$$\text{PE of electron} = -2KE = \frac{-e^2 Z^2}{4\pi\epsilon_0 r_n} = -27.2 \frac{Z^2}{n^2} \text{ eV}$$

Binding energy of electron $BE = E_n = KE + PE$

$$= \frac{-e^2 Z^2}{8\pi\epsilon_0 r_n} = -13.6 \frac{Z^2}{n^2} \text{ eV}$$

$$\text{Ionization potential } \frac{E_n}{e} = 13.6 \frac{Z^2}{n^2} \text{ Volt}$$

$$\text{Rydberg constant } R = \frac{me^4}{8\epsilon_0^2 ch^3} = 1.09737 \times 10^7 \text{ m}^{-1}$$

Ionization energy is the minimum energy required for an electron so that it loses its ground state and reaches vacuum level or continuum, or it is relieved from binding of the nucleus.

Excitation energy is the minimum energy required for an electron to jump to a higher energy state.

Hydrogen Spectrum

$$\text{Rydberg's empirical relation } \frac{1}{\lambda} = R \left[\frac{1}{n^2} - \frac{1}{m^2} \right]$$

Wave number $\bar{\nu} = \frac{1}{\lambda}$ defines the number of waves per unit length.

$$\therefore \text{Number of waves in a distance } d \text{ is } N = \frac{d}{\lambda}$$

Lyman series

$$\frac{1}{\lambda} = R \left[\frac{1}{1^2} - \frac{1}{n^2} \right] \quad n = 2, 3, \dots$$

$$\lambda_{\max} = 1216 \text{ \AA}; \lambda_{\min} = 912 \text{ \AA}$$

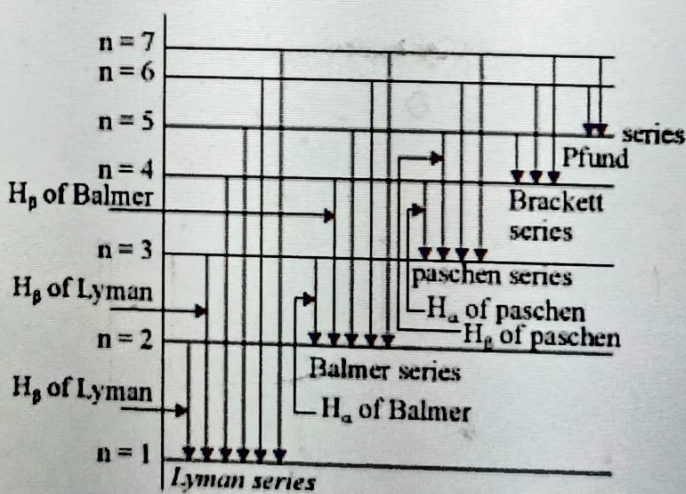


Fig. 18.3 Hydrogen spectrum

This series lies in uv region. It shows both emission and absorption spectrum.

Note: Transitions occur from higher energy states to ground state.

Balmer series In this series, transitions occur from higher energy states to $n = 2$ or 1st excited state.

$$\frac{1}{\lambda} = R \left[\frac{1}{2^2} - \frac{1}{n^2} \right] \quad n = 3, 4, 5, \dots$$

This series lies in visible region. It shows only emission spectrum.

$$\lambda_{\max} = 656.3 \text{ nm}, \lambda_{\min} = 364.6 \text{ nm}$$

Paschen series The transitions occur from higher energy levels D to $n = 3$

$$\frac{1}{\lambda} = R \left[\frac{1}{3^2} - \frac{1}{n^2} \right] n = 4, 5, 6, \dots$$

This series lies in IR region with $\lambda_{\max} = 1875.1 \text{ nm}$ and $\lambda_{\min} = 810.7 \text{ nm}$. Only emission spectrum is shown.

Brackett series The transitions from higher energy states to $n = 4$ result into Brackett series

$$\frac{1}{\lambda} = R \left[\frac{1}{4^2} - \frac{1}{n^2} \right] n = 5, 6, \dots$$

The minimum and maximum wavelengths of the series are $\lambda_{\max} = 4047.7 \text{ nm}$ $\lambda_{\min} = 1457.2 \text{ nm}$. It lies in deep IR region and shows only emission spectrum.

Pfund series The transition from higher levels to $n = 5$ result into Pfund series.

$$\frac{1}{\lambda} = R \left[\frac{1}{5^2} - \frac{1}{n^2} \right] n = 6, 7, \dots$$

$\lambda_{\max} = 7451.5 \text{ nm}$ and $\lambda_{\min} = 2276.8 \text{ nm}$. The series appears in deep IR region and shows only emission spectrum.

The number of spectral lines emitted $N = \frac{n(n-1)}{2}$ if electron lies in n th state

Pauli's exclusion principle No two electrons can occupy all the four quantum number equal. It describes in a subshell electron must be oriented in opposite spins and hence, favours diamagnetism as the law of nature.

Fermions The particles which follow Pauli's exclusion principle or Fermi-Dirac statistics are called Fermions. Electrons, neutrons, protons etc are Fermions. They have spin $(2n + 1) \frac{h}{2}$ or half odd multiple of h .

Bosons The particles which follow Bose-Einstein statistics are called Bosons. Bosons have spin $n h$ where n is an integer. Photons, Gravitons, Phonons excitons, cooper pair etc. are Bosons.

Short Cuts and Points to Note

1. Bohr model could not explain Hydrogen spectrum completely what to talk of other atoms or hydrogen like atoms i.e. He^+ , Li^{++} etc. 656.3 nm line in H -spectrum was found to split in 5 lines. No explanation for such a splitting is given in Bohr's model. Bohr arbitrarily assumed that orbits are stationary. He gave no reason as to why the moving charge do not lose energy. It could not even explain Zeeman and Stark effects.

According to Bohr's Theory

2. Radius of n th orbit $r_n = n^2 (0.53) \text{ \AA}$ for Hydrogen.

$$r_n = \frac{n^2}{Z} (0.53) \text{ \AA} \text{ for hydrogen like atoms}$$

3. Velocity of electron in n th orbit $v_n = \frac{2.2 \times 10^6}{n} \text{ ms}^{-1}$

$$\text{for hydrogen } v_n = \frac{2.2 \times 10^6}{n} \text{ ms}^{-1} \text{ for hydrogen like atoms.}$$

4. Angular frequency $\omega_n = \frac{4.159 \times 10^6}{n^3} \text{ rads}^{-1}$ for hydrogen.

$$\omega_n = \frac{4.159 \times 10^6 Z^2}{n^3} \text{ rads}^{-1} \text{ for hydrogen like atoms.}$$

5. Linear frequency $f = \frac{6.625 \times 10^5 Z^2}{n^3} \text{ s}^{-1}$

6. Time period of revolution $T_n = \frac{1.5 \times 10^{-6} n^3}{Z^2} \text{ s}$

7. Electric current due to an electron motion in the n th

$$\text{orbit } I_n = \frac{1.06 Z^2}{n^3} \text{ mA.}$$

8. Magnetic induction $B_n = \frac{12.58 Z^3}{n^3}$ Tesla reduce for electron revolving in n th orbit.

9. Magnetic moment $M_n = \frac{eh}{2m} = \frac{eh}{4\pi m} = 9.26 \times 10^{-24}$

Am^2 for the first orbit of hydrogen and is called Bohr magneton. In n th orbit $M_n = n M = n \times 9.26 \times 10^{-24} \text{ Am}^2$.

10. Potential Energy, $PE = -2 KE$

$$KE = \frac{13.6Z^2}{n^2} eV \quad PE = \frac{-27.2Z^2}{n^2} eV.$$

$$\text{Binding energy } BE = KE + PE = -13.6 \frac{Z^2}{n^2} eV.$$

11. Ionization potential = $\frac{13.6Z^2}{n^2}$ Volt.

12. Rydberg constant $R = 1.09737 \times 10^7 m^{-1}$

$Rhc = -13.6 eV$ in terms of energy

13. Excitation potential = $-13.6 Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$.

14. Lyman series in the Hydrogen spectrum shows both emission and absorption spectrum. All other series of Hydrogen spectrum show emission spectrum.

15. n th excited state means $(n + 1)$ th energy level or orbit.

16. Maximum number of spectral lines which could be emitted when electron is in the n th state = $\frac{n(n-1)}{2}$.

17. The energy level difference goes on decreasing as n increases.

18. Total number of elements for a given principal quantum number n is

$$= 2[n^2 + (n-1)^2 + \dots + 1^2]$$

For example, for $n = 3$.

$$\text{Total number of elements} = 2[3^2 + 2^2 + 1^2] = 28$$

19. Distance of closest approach in α -particle scattering

$$r = \frac{2Ze^2}{4\pi\epsilon_0(KE)} \text{ and}$$

$$\text{impact parameter } b = \frac{Ze^2 \cot\left(\frac{\theta}{2}\right)}{4\pi\epsilon_0(KE)}$$

Number of particles scattered at an angle θ

$$N(\theta) \propto \frac{Z^2}{\sin^4\left(\frac{\theta}{2}\right)(KE)^2}$$

20. λ (nm) = $\frac{1240}{E(eV)} = \frac{1240}{E_2 - E_1}$ for absorption or emission of radiation.

21. If in Bohr's theory, instead of m (mass of electron),

reduced mass $m_r = \frac{m_p m_e}{m_p + m_e}$ is taken ($m_e \rightarrow$ mass of proton, $m_p \rightarrow$ mass of electron) then a perfect result is obtained).

22. X-rays may be divided into two categories: soft X-ray and hard X-ray. Soft X-rays are mainly used in medical science. (Frequency $\sim 10^{16}$ Hz). Hard X-rays have wave length 0.1 \AA to 10 \AA and is mainly used in industry. (frequency $\sim 10^{18}$ Hz)