Chapter 12

Atoms

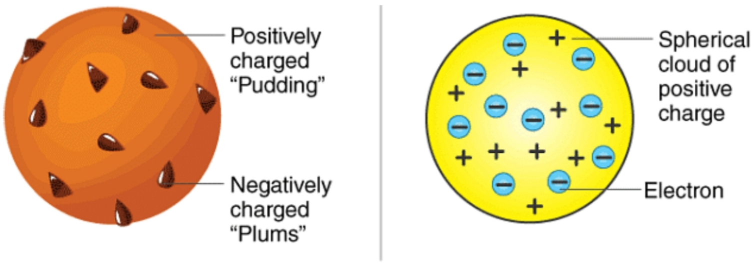
Rutherford's Nuclear Model of an Atom

Dalton's Atomic Theory

All elements are consists of very small invisible particles, called atoms. Atoms of same element are exactly same and atoms of different element are different.

Thomson's Atomic Model

Every atom is uniformly positive charged sphere of radius of the order of 10^{-10} m, in which entire mass is uniformly distributed and negative charged electrons are embedded randomly. The atom as a whole is neutral.



Thomson's atomic model

Limitations of Thomson's Atomic Model

- It could not explain the origin of spectral series of hydrogen and other atoms.
- It could not explain large angle scattering of α – particles.

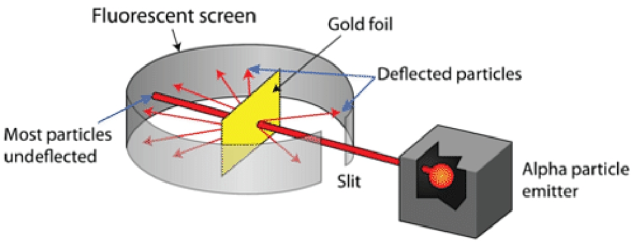
Rutherford's Atomic Model

<u>On the basis of this experiment, Rutherford made following observations:</u>

- The entire positive charge and almost entire mass of the atom is concentrated at its centre in a very tiny region of the order of 10^{-15} m, called nucleus.
- The negatively charged electrons revolve around the nucleus in different orbits.

- The total positive charge 011 nucleus is equal to the total negative charge on electron. There fore atom as a overall is neutral.

The centripetal force required by electron for revolution is provided by the electrostatic force of attraction between the electrons and the nucleus.



Rutherford's Atomic Model

Distance of Closest Approach

$r_o = 1 / 4\pi \varepsilon_o . 2Ze^2 / E_k$
where, E_k = kinetic energy of the cc-particle.

Impact Parameter

The perpendicular distance of the velocity vector of a-particle from the central line of the nucleus, when the particle is far away from the nucleus is called impact parameter.
Impact parameter

$$b = \frac{1}{4\pi \varepsilon_0} \cdot \frac{Ze^2 \cot\left(\frac{\theta}{2}\right)}{E_k}$$

where, Z = atomic number of the nucleus, E_k = kinetic energy of the c-particle and θ = angle of scattering.

Rutherford's Scattering Formula

$$N(\theta) = \frac{N_i nt Z^2 e^4}{(8\pi\varepsilon_0)^2 r^2 E^2 \sin^4\left(\frac{\theta}{2}\right)}$$

where, $N(\theta)$ =number of c-particles, N_i = total number of α-particles reach the screen. n = number of atoms per unit volume in the foil, Z = atoms number, E = kinetic energy of the alpha particles and t = foil thickness

$$N \propto \frac{1}{\sin^4\left(\frac{\theta}{2}\right)}$$

Limitations of Rutherford Atomic Model

- **About the Stability of Atom:** According to Maxwell's electromagnetic wave theory electron should emit energy in the form of electromagnetic wave during its orbital motion. Therefore. radius of orbit of electron will decrease gradually and ultimately it will fall in the nucleus.
- **About the Line Spectrum:** Rutherford atomic model cannot explain atomic line spectrum

Bohr's Atomic Model & Electron Orbits

Bohr's Atomic Model

Electron can revolve in certain non-radiating orbits called stationary or bits for which the angular momentum of electron is an integer multiple of $(h / 2\pi)$
$mvr = nh / 2\pi$
where n = I, 2. 3 called principle quantum number.
The radiation of energy occurs only when any electron jumps from one permitted orbit to another permitted orbit.
Energy of emitted photon
$hv = E_2 - E_1$
where E_1 and $E_2$are energies of electron in orbits.

Radius of orbit of electron is given by
$r = n^2h^2 / 4\pi^2 mK Ze^2 \Rightarrow r \propto n^2 / Z$
where, n = principle quantum number, h = Planck's constant, m = mass of an electron, $K = 1 / 4 \pi \varepsilon$, Z = atomic number and e = electronic charge.

Velocity of electron in any orbit is given by
$v = 2\pi KZe^2 / nh \Rightarrow v \propto Z / n$

Frequency of electron in any orbit is given by
$v = KZe^2 / nhr = 4\pi^2Z^2e^4mK^2 / n^3 h^3$
⇒ v prop; Z^3 / n^3

Kinetic energy of electron in any orbit is given by
$E_k = 2\pi^2 me^4 Z^2 K^2 / n^2 h^2 = 13.6\ Z^2 / n^2$ eV

Potential energy of electron in any orbit is given by
$E_p = -\ 4\pi^2 me^4 Z^2 K^2 / n^2 h^2 = 27.2\ Z^2 / n^2$ eV
$\Rightarrow E_p = \propto Z^2 / n^2$

Total energy of electron in any orbit is given by
$E = -\ 2\pi^2 me^4 Z^2 K^2 / n^2 h^2 = -\ 13.6\ Z^2 / n^2$ eV
$\Rightarrow E_p = \propto Z^2 / n^2$
Wavelength of radiation emitted in the radiation from orbit n_2 to n_1 is given by

$$\frac{1}{\lambda} = \frac{2\pi^2 m K^2 e^4 Z^2}{ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

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

$$R = \frac{2\pi^2 m K^2 e^4 Z^2}{ch^3}$$

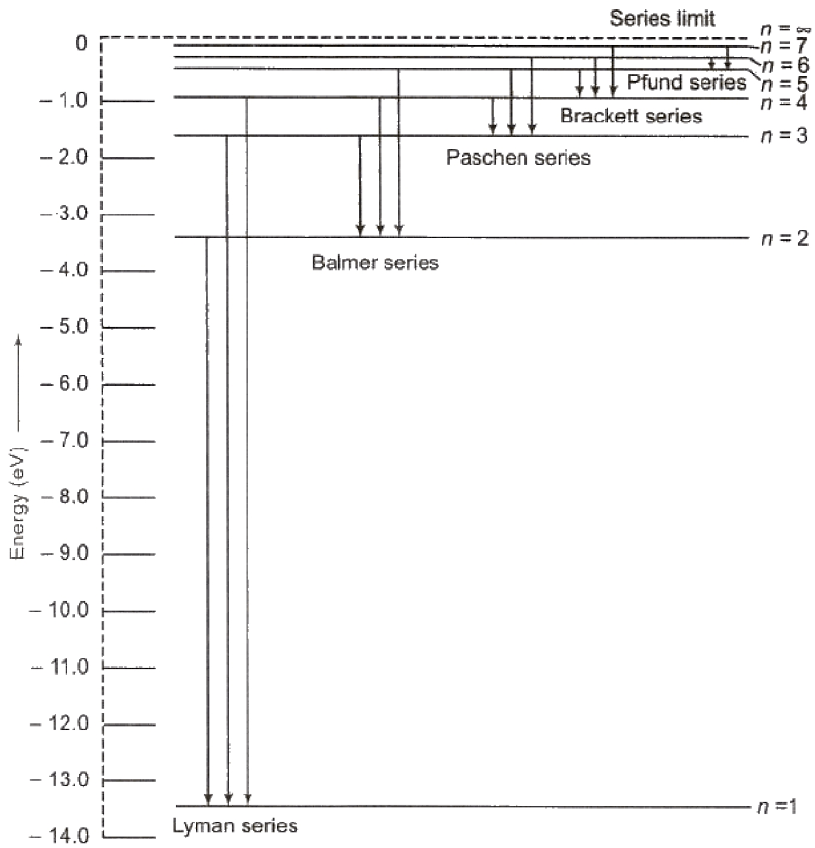
$$= 1.097 \times 10^7\ \text{m}^{-1}$$

In quantum mechanics, the energies of a system are discrete or quantized. The energy of a particle of mass m is confined to a box of length L can have discrete values of energy given by the relation
$E_n = n^2 h^2 / 8mL^2;\ n < 1, 2, 3,$

Hydrogen Spectrum Series

Hydrogen Spectrum Series

Each element emits a spectrum of radiation, which is characteristic of the element itself. The spectrum consists of a set of isolated parallel lines and is called the **line spectrum.**



Hydrogen spectrum contains five series

(i) **Lyman Series** When electron jumps from n = 2, 3,4, ...orbit to n = 1 orbit, then a line of Lyman series is obtained.

This series lies in ultra **violet region.**

(ii) **Balmer Series** When electron jumps from n = 3, 4, 5,... orbit to n = 2 orbit, then a line of Balmer series is obtained.

This series lies in **visual region.**

(iii) **Paschen Series** When electron jumps from n = 4, 5, 6,... orbit to n = 3 orbit, then a line of Paschen series is obtained.

This series lies in **infrared region**

(iv) **Brackett Series** When electron jumps from n = 5,6, 7.... orbit to n = 4 orbit, then a line of Brackett series is obtained.

This series lies in **infrared region.**

(v) **Pfund Series** When electron jumps from n = 6,7,8, ... orbit to n = 5 orbit, then a line of Pfund series is obtained.

This series lies in **infrared region.**

Wave Model

It is based on wave mechanics. Quantum numbers are the numbers required to completely specify the state of the electrons.
In the presence of strong magnetic field, the four quantum number are
(i) Principle quantum number (n) can have value 1,2, ... ∞
(ii) Orbital angular momentum quantum number l can have value 0,1, 2 (n – 1).
(iii) Magnetic quantum number (m_e) which can have values – I to I.
(iv) Magnetic spin angular momentum quantum number (m_s) which can have only two value + 1 / 2.

De Broglie's Explanation of Bohr's Second Postulate of Quantisation

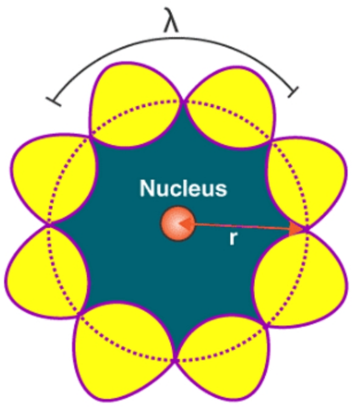
Angular Momentum Of Electron

What is Angular Momentum of Electron?

Angular momentum of an electron by Bohr is given by mvr or nh/2π (where v is the velocity, n is the orbit in which electron is, m is mass of the electron, and r is the radius of the nth orbit).
Bohr's atomic model laid down various postulates for the arrangement of electrons in different orbits around the nucleus. According to Bohr's atomic model, the angular momentum of electron orbiting around the nucleus is quantized. He further added that electrons move only in those orbits where angular momentum of an electron is an integral multiple of h/2. This postulate regarding the quantisation of angular momentum of an electron was later explained by Louis de Broglie. According to him, a moving electron in its circular orbit behaves like a particle wave.

De Broglie's Explanation to the Quantization of Agular Momentum of Electron:

The behaviour of particle waves can be viewed analogously to the waves travelling on a string. Particle waves can lead to standing waves held under resonant conditions. When a stationary string is plucked, a number of wavelengths are excited. On the other hand, we know that only those wavelengths survive which form a standing wave in the string, that is, which have nodes at the ends.



Quantization of Angular Momentum of Electron

Thus, in a string, standing waves are formed only when the total distance travelled by a wave is an integral number of wavelengths. Hence, for any electron moving in kth circular orbit of radius rk, the total distance is equal to the circumference of the orbit, 2πrk.

$$2\pi r_k = k\lambda$$

Let this be equation (1).

Where,

λ is the de Broglie wavelength.

We know that de Broglie wavelength is given by:

$$\lambda = h/p$$

Where,

p is electron's momentum

h = Planck's constant

Hence,

$$\lambda = h/mv_k$$

Let this be equation (2).

Where mv_k is the momentum of an electron revolving in the k^{th} orbit. Inserting the value of λ from equation (2) in equation (1) we get,

$$2\pi r_k = kh/mv_k$$

$$mvkr_k = kh/2\pi$$

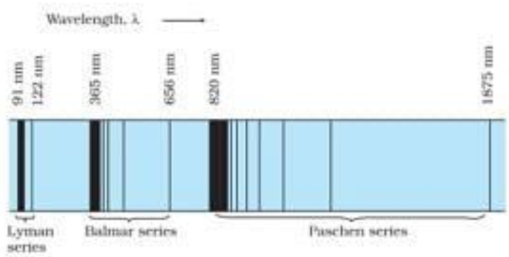
Hence, de Broglie hypothesis successfully proves Bohr's second postulate stating the quantization of angular momentum of the orbiting electron. We can also conclude that the quantized electron orbits and energy states are due to the wave nature of the electron.

Atomic Spectra

All condensed matter (solids, liquids, and dense gases) emit electromagnetic radiation at all temperatures. Also, this radiation has a continuous distribution of several wavelengths with different intensities. This is caused by oscillating atoms and molecules and their interaction with the neighbours. In the early nineteenth century, it was established that each element is associated with a characteristic spectrum of radiation, known as Atomic Spectra. Hence, this suggests an intimate relationship between the internal structure of an atom and the spectrum emitted by it.

Atomic Spectra

When an atomic gas or vapour is excited under low pressure by passing an electric current through it, the spectrum of the emitted radiation has specific wavelengths. It is important to note that, such a spectrum consists of bright lines on a dark background. This is an emission line spectrum. Here is an emission line spectrum of hydrogen gas:



Emission lines in the spectrum of hydrogen

The emission line spectra work as a 'fingerprint' for identification of the gas. Also, on passing a white light through the gas, the transmitted light shows some dark lines in the spectrum. These lines correspond to those wavelengths that are found in the emission line spectra of the gas. This is the absorption spectrum of the material of the gas.

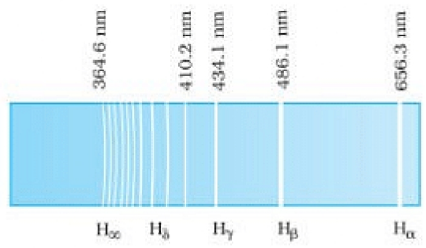
Spectral Series of Atomic Spectra

Normally, one would expect to find a regular pattern in the frequencies of light emitted by a particular element. Let's look at hydrogen as an example. Interestingly, at the first glance, it is difficult to find any regularity or order in the atomic spectra. However, on close observation, it can be seen that the spacing between lines within certain sets decreases in a regular manner. Each of these sets is a spectral series. Five spectral series identified in hydrogen are

1. Balmer Series
2. Lyman Series
3. Paschen Series
4. Brackett Series
5. Pfund Series

Further, let's look at the Balmer series in detail.

1. Balmer Series



Balmer series in the emission spectrum of hydrogen

In 1885, when Johann Balmer observed a spectral series in the visible spectrum of hydrogen, he made the following observations:

- The longest wavelength is 656.3 nm
- The second longest wavelength is 486.1 nm
- And the third is 434.1 nm
- Also, as the wavelength decreases the lines appear closer together and weak in intensity
- He found a simple formula for the observed wavelengths:

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

where λ is the wavelength
R is the Rydberg's constant and
n can have any integral value.

Further, for n=∞, you can get the limit of the series at a wavelength of 364.6 nm. Also, you can't see any lines beyond this; only a faint continuous spectrum. Furthermore, like the Balmer's formula, here are the formulae for the other series:

2. Lyman Series

$$\frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right)$$

where λ is the wavelength
R is the Rydberg's constant and
n can have any integral value.

3. Paschen Series

$$\frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$$

where λ is the wavelength
R is the Rydberg's constant and
n can have any integral value

4. Brackett Series

$$\frac{1}{\lambda} = R\left(\frac{1}{4^2} - \frac{1}{n^2}\right)$$

where λ is the wavelength
R is the Rydberg's constant and
n can have any integral value

5. Pfund Series

$$\frac{1}{\lambda} = R\left(\frac{1}{5^2} - \frac{1}{n^2}\right)$$

where λ is the wavelength
R is the Rydberg's constant and
n can have any integral value