# Atomic Structure

1. **Bohr's theory of Hydrogen like atoms**:-

(Bohr postulates):

(i) An atom consists of positively charged nucleus responsible for the entire mass of the atom.

(ii) Electrons revolve around the nucleus in certain permitted circular orbits of definite radii

(iii) The permitted orbits are those for which the angular momentum of an electron is an integral multiple of $h/2\pi$, where h = Planck's constant

If m is the mass and Vis the velocity of the electron in a permitted orbit of radius, then $L = mvr = n(h/2\pi); n = 1, 2, 3$

n = principal quantum number. This equation is known as the Bohr quantization postulate.

(iv) When electrons move in postulate permitted discrete orbits they do not radiate energy. Such orbits are called stationary or non-radiating orbits.

(v) The energy is radiated when the electron jump from higher to lower orbit and the energy is absorbed when it jumps from lower to higher orbit.

It $E_i$&$E_f$ are the energies associated with orbits of principal quantum numbers $n_i$and $n_f$ respectively ($n_i$<$nr_f$) the frequency of the radiation emitted is given by

$hv = \Delta E = E_q - E_i \rightarrow$ Bohr frequency condition

Let the charge on nucleus be + ze. The electron with charge –e revolves around the nucleus of radius r with velocity. v. The electrostatic force of attraction between nucleus & electrons is given by

$$F_c = \frac{1}{4\pi\varepsilon\partial}\frac{Ze^2}{r^2}$$

Centripetal force, Fe, acquired by the electron is given by

$$F_C = \frac{mv^2}{r}$$

$$F_C = F_C$$

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

$$\Rightarrow mv^2 = (1/4\pi\varepsilon_{-0})\left(\frac{Ze^2}{r}\right) - (1)$$

According to Bohr quantization condition

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

$$n = 1, 2, 3$$

$$\text{or, } v = \frac{nh}{2\pi mr} - (2)$$

Substituting for vin eqn. (1) we have

$$m\left(\frac{nh}{2\pi mr}\right)^2 = (1/4\pi\varepsilon_o)(Ze^2/r)$$

Hence the radius $r_n$ of the $n^{th}$orbit is given by

$$r_n = \left(\frac{\varepsilon_0 h^2}{\pi m e^2}\right)\frac{n^2}{z}$$

$$=\left(0.529\,\text{Å}\right)$$

## 1.1. Energy of the electron:

Let Ek&Ep be the k. E. and the P.E. respectively, of the electron in nth orbit. Then the total energy is equal to sum of Ek and Ep i.e.

$$E = Ek + Ep = \frac{1}{2}mv^2 - \frac{ze^2}{4\pi\varepsilon_o r}\left[-\text{ve sign due to attraction}\right]$$

From equation –(1) $mv^2 = \frac{1}{4\pi\varepsilon_o}\left(\frac{ze^2}{r}\right)$ : condition of stationary orbit

$$Ek = \frac{1}{4\pi\in o}\frac{\cancel{z}e^2}{2r}$$

Hence:

$$E = \frac{1}{4\pi\varepsilon_0}\frac{\cancel{z}e^2}{2r} - \frac{1}{4\pi\varepsilon_0}\frac{\cancel{z}e^2}{r}$$

$$= \frac{-1}{4\pi\varepsilon_0}\frac{\cancel{z}e^2}{2r} - (3)$$

Substituting value of r from above

$$E_n = -\left(\frac{1}{4\pi\varepsilon_0}\right)^2\frac{2\pi^2 z^2 m e^4}{n^2 h^2}$$

$$E_n = \frac{-me^4}{8{\varepsilon_0}^2 h^2}\left(\frac{\cancel{z}^2}{h^2}\right)$$

$$E_n = \left(-13.6\,\text{eV}\right)\frac{z^2}{n^2}$$

First hydrogen atom

E = -13.6 ev

**Note :**Energy of the electron in n = 1 orbit is called ground state energy. n = 2 called first excited state.

## 1.2. Spectrum of Hydrogen atom:

Spectrum arises when an electron in the intialsiationary orbit of principal quantum number$n_i$jumps to the final stationary orbit of principal quantum number $n_f$($n_i$>$n_f$) so that difference of the energy associated with these orbits is emitted as a photon of frequency v accordingly

hv = $E_i$-$E_f$

$$= -\left(\frac{1}{\left(4\pi\varepsilon_0\right)^2}\right)^2\frac{2\pi^2 z^2 m e^4}{{n_i}^2 h^2} - \left(\frac{-1}{\left(4\pi\varepsilon_0\right)^2}\right)\frac{2\pi^2 z^2 m e^4}{{n_f}^2 h^2}$$

$$hv = \frac{1}{\left(4\pi\varepsilon_0\right)^2}\frac{2\pi^2 m e^4}{h^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)z^2$$

Or $v = \frac{C}{\lambda}$

$$\frac{hc}{\lambda} = \left(\frac{1}{4\pi\varepsilon_0}\right)^2 \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{n^2 f} - \frac{1}{n_i^2}\right)z^2$$

$$\text{or} = \frac{1}{\lambda} = \left(\frac{1}{4\pi\varepsilon_0}\right)^2 \frac{2\pi^2 me^4}{h^3 c}\left(\frac{1}{n^2 f} - \frac{1}{n_i^2}\right)z^2 = \tilde{v}$$

## 2. Particle and wave character:

Einstein had suggested that light has dual character; as wave and also as particle.

Louis de Broglie suggested proposed that matter also has a dual character; as wave and as particle.

## 2.1. Derivation:

De Broglie equation can be easily deived by using mass-energy relationship viz.

Equating this energy with the energy of a photon, me have hv = $mc^2$

Since

$$v = \frac{c}{\lambda}$$

$$\frac{hc}{\lambda} = mc^2$$

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

Replacing c by the velocity of the electron $v_1$ we have

$\pi = h / mv = h / p$

Where p is the momentum of electron

waves& electromagnetic waves:

(i) Speeds of matter waves are not same as that electromagnetic waves. It is less. EM waves travel with speed c.

(ii) Matter waves can not be radiated in empty space.

(iii) Wave length of matter waves are generally very small as compared to the wavelength of electromagnetic waves.

Derivation of the Bohr angular momentum postulate from de Broglie's relation. Electron moving in a circular orbit of radiusr around a nucleus Evidently if the wave is to reamin continually in phase, the circumference of the circular orbit must be an integral multiple of the wavelength $\lambda$, that is

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

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

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

**Q.**What is wavelength of the electron in the $n^{th}$Bohrorbit. [for Hydrogen atom]

**Ans.**circumference of the orbit is an integral multiple of wavelengths i.e. $2\pi r = n\lambda$ Furtherrodivs of the orbit is directly proportional to $n^2$ therefore $2\pi r$ is proportional to n2. Incase of Hydrogen, the radivs of the first orbit is $0.529A^0$ the radius of the $n^{th}$

orbit =
(0.529×$n^2$) $A^{0.}$ Thearuemference of this orbit is

$$2\pi r_n = 2\pi \times 0.529 n^2$$

$$n\lambda = 2\pi \times 0.529 n^2$$

$$\lambda = (0.529 \times 2\pi) n \ (\text{Å})$$

## 3. Heisenberg's uncertainty principle:

Also called principle of indeterminancy& it is the fundamental basis of quantum mechanics.

## 3.1. Popular statement:

It is not possible to determine simultaneously and precisely the momentum and the position of
amicroscopic particle. According to Heisenberg the product of uncertainty in these quantities
is givenas $\Delta p.\Delta x \geq \frac{h}{4\pi}$ inother words the product $\Delta p.\Delta x$ is of the order of the Planck's const.
In case of macroscopic body the wavelength is extremely small, so that uncertainty is little
It is impossible to specify simultaneously with orbital precision, both the momentum and the position of a particle, and more generally any pair of observables with operators that do not commute.

$$\Delta J\ \Delta\theta \geq \frac{\hbar}{2}, \Delta E \Delta t \geq \frac{\hbar}{2}$$

- Quantitatively, $\Delta p\ \Delta x \geq \frac{\hbar}{2}$ [It is derived by combining de Broglie relation $\lambda = \frac{h}{p}$ and Einstein relation $E = hv$]

Where $\Delta p$ is the 'uncertainty' in linear momentum. Parallel to the axis x, and $\Delta x$ is the
uncertainty in position along that axis.
These 'uncertainties' are precisely defined, for they are the root mean square deviations of the properties from their mean values

$$\Delta p = \left\{< p^2 > - < p >^2\right\}^{\frac{1}{2}} \text{ and } x = \left\{< x^2 > - < x >^2\right\}^{\frac{1}{2}}$$

If there is complete certainty about the position of the particle (Δx=0), then there will be
complete uncertainty about momentum.
Conversely, if the momentum parallel to an axis is known exactly (Δp=0), then the
position along that must be completely uncertain (Δx=0).
Whereas simultaneous specification of the position on the x-axis and momentum
parallel to the x-axis are restricted by the uncertainty relation, simultaneous location of position on x and motion parallel to y or z are not restricted.
For any two observables which do not commute we have

$$\Delta A\ \Delta B \geq \frac{1}{2}\left|< [A, B] >\right|$$

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It is important to realize that the uncertaintsys relations are not experimental errors that are dependent in the quantity of measurement apparatus, but are inherent in quantum mechanics. Because of this uncertainty the results of quantum mechanical calculations are expressed in terms of probabilities.

The de-Broglie wave length of macro scopic systems is extremely small so the uncertainty is negligible, for all practical purposes, for macroscopic systems.

For ex:

A projectile of 1 gm with speed 1 $\mu m/sec$ then calculate the uncertainty in its position.

$$\Delta x = \frac{\hbar}{2m\Delta v} = 5\times10^{-26} m.$$

**Example:**

What must be the mass of a particle which must provide a binding for the nucleons within

Assume velocity of particle = c If $\Delta x$ is the size of the nucleus then velocity of particle is

$$c = \frac{\Delta x}{\Delta t}$$

$$\Delta t = \frac{\Delta x}{c}$$

$$\Delta E \times \Delta t \approx h/4\pi$$

Further $\therefore \Delta E \times \frac{\Delta x}{c} \approx h/4\pi$

If the mass of the particle is m, then

$$\Delta E \approx mc^2$$

$$(mc^2)\times\frac{\Delta x}{c} \approx h$$

$$\therefore m \approx \frac{h}{c\Delta x\, 4\pi}$$

$$= 2.2\times10^{-24} \text{ gm.}$$

$$\frac{m}{me} = \frac{22\times10^{-24}}{9\times10^{-28}} = \frac{2.2\times10^{4}}{9} \approx 2444$$