B. Sc. Part-II (Sub) Chemistry, Paper-II, Group-B (Inorganic)
Unit-1 Atomic Structure. [By Dr. Birendra Kumar, Maharaja college]

⟹ de-Broglie's wave equation / Wave-Particle dualism:

Louis de-Broglie, a French physicist advanced the hypothesis that all forms of matter (microscopic) like electron, proton, neutron, atom, molecule etc show dual characters, i.e, particle (corpuscular) as well as wave nature. The wave associated with such particles is called a 'matter wave' which is different from electromagnetic wave.

He gave correlation between momentum (particle nature) and wavelength (wave nature) of a moving electron/particle in the form of an equation, known as de-Broglie's wave equation. According to the relation, $\lambda = \frac{h}{mv} = \frac{h}{p}$ — (1)

(Where λ = wavelength of matter wave, p = momentum, m = mass of particle, v = velocity)

* Derivation: The de-Broglie equation can be easily derived by using Einstein mass-energy relationship. Consider the case of an electron. If it is supposed to have wave nature, its energy will be given by. $E = h\nu$ (Planck's equation)

Or, $E = \frac{hc}{\lambda}$ — (2) [Since $c = \nu\lambda$ or $\nu = c/\lambda$]

(Where E = Energy, ν = frequency of electronic wave, λ = wavelength, c = velocity of light, h = Planck's con

On the other hand, if electron is supposed to have particle nature, its energy is given by Einstein mass-energy relation, $E = mc^2$ — (3)

From equation (2) & (3), $\frac{hc}{\lambda} = mc^2$ or, $\lambda = \frac{h}{mc} = \frac{h}{p}$ [$\because$ p (momentum) = mass × velocity (mc)]

This is the de-Broglie's wave equation.

* Limitations: (i) It is true only for microscopic particles (e.g; e, p, n).
(ii) It has no relevance for moving semi micro or macro particles, e.g. ball.

* Evidences to support wave and particle nature or dual nature of electron:

For particle nature: (i) It has all characteristics of particle: mass, charge, energy and also momentum (ii) when strikes a ZnS coated plate/screen, a bright spot (scintillation) is produced (iii) Black body radiation and photo electric effect.

For wave nature: (i) Davisson & Germer experiment (ii) Thomson experiment.

⟹ Heisenberg Uncertainty principle:

In 1927, Werner Heisenberg, a German physicist developed the uncertainty principle which is an important consequences of the dual nature of microscopic particles, e.g. electron. It stated as "It is impossible to measure simultaneously both the position and momentum of a microscopic particle (e.g; electron) with absolute accuracy or certainty."

The product of uncertainty (or error in measurement) in position and uncertainty in momentum of a microscopic particle is always constant and is equal to or greater than $h/4\pi$, i.e; $\Delta x \cdot \Delta p \geq h/4\pi$ or, $\Delta x \cdot m \times \Delta v \geq h/4\pi$ — (1)

(where Δx = uncertainty or error in determining its position, Δp = uncertainty in measuring momentum, Δv = uncertainty in measuring velocity, m = mass of particle).

From equation (1), it is evident that if Δx is small, i.e; the position of the particle is known almost exactly, Δp or Δv would be large, i.e; there would be large uncertainty or error in its measured value. This principle has no impact on our daily life since it is concern with microscopic particles, not macro particles.

⇒ Schrodinger's wave equation:

In 1926, Erwin Schrodinger profased that since an electron behave as a wave, it should obey the same equation of motion which all other known types of waves obey. On the basis of this simple idea, he derived an equation which describes the wave motion of an electron-wave propagating in three dimensions (x, y & z) in space. This wave equation is called schrodinger's wave equation. This is written in different forms:

1. Cartesian coordinates form: $\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$ —— (1)

[Where ψ = wave function and represent the amplitude of wave, m = mass of particle (electron), E = total energy of the particle describing wave motion, V = Potential energy of particle due to position, h = Planck's constant (6.6×10^{-34} J), π = a constant (3.141)]

2. Polar coordinate form:

$$\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\cdot\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\cdot\frac{\partial^2}{\partial\phi^2}\right]\psi+\frac{8\pi^2 m r^2}{h^2}(E-V)\psi=0 \quad \text{—— (2)}$$

[Where r, θ & φ are polar coordinates]

⇒ Wave function:

Wave function represents the amplitude of wave. It is denoted by symbol ψ (psi). From the wave function almost all physically observable proferty of a dynamic particle can be described. It has no physical significance, since it cannot represent the probability of finding an electron in a small volume around the nucleus. This is because of the fact that the wave function (ψ) can have positive as well as negative values, whereas the probability of finding the electron can be zero or positive but can never be negative. However, ψ^2 represents or measures the probability of finding the electron around the nucleus. Its value is always positive. The probability or chance of finding an electron in space around the nucleus is called electron probability function ($\mathcal{P}$). The value of $\mathcal{P}$ for an extremely small spherical shell of radius (r) and thickness (dr) around the nucleus is given by, $\mathcal{P}=\psi^2\times$ volume of spherical shell $=4\pi r^2 dr\cdot\psi^2$

Thus, the electron probability between r=0 & r=r could be, $\int_{r=0}^{r=r}\psi^2 4\pi r^2 dr$.

⇒ Eigen function & Eigen value:

Schrodinger wave equation, being a differential equation of second order, has many solutions. Some of these values are imaginary (non-acceptable) while others are real values. Only those values of ψ which give definite and acceptable value of the total energy (E) of the electron. These acceptable values of wave function (ψ) are called eigen (acceptable) wave functions. The value of total energy (E) given by a particular eigen wave function is called eigen value.

The acceptable wave functions fulfill following conditions:

(i) ψ must be single valued solution, i.e., if one of variable is θ, then $\psi(\theta)=\psi(\theta+2n\pi)$

(ii) ψ must finish at infinity for bound system, and must satisfy the relation:

$$\int|\psi^2|\,d\tau=1$$

(iii) ψ and its first derivative with respect to its variables are finite and continuous.

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