Group-A: Unit-1 Atomic structure

Schrodinger's wave equation:

In 1926, Ervin Schrodinger proposed 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:

(A) Cartesian coordinates form:

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0 \quad \text{——} (1)$$

[Where ψ = wave function & represent the amplitude of wave. From the wave function almost all physically observable property of a dynamic particle can be described. Its square (ψ^2) has a physical meaning related to probability., 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 ($6.6\times10^{-34}J$), π = a Constant (3.141)]

(B) In term of Laplacian Operator:

$$\nabla^2\psi+\frac{8\pi^2 m}{h^2}(E-V)\psi=0 \quad \text{——} (2)$$

(Where $\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$, Called laplacian mathematical operator)

$\nabla^2\psi$ should not mean that ∇^2 is multiplied by ψ. x, y & z are the three space coordinates of the electron with respect to nucleus (0,0,0). Here $\partial^2\psi/\partial x^2$ is double differential of $\psi(x,y,z)$ with respect to x only keeping y & z constant.

(C) In term of Hamiltonian operator:

We have, $\nabla^2\psi+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$ or, $\nabla^2\psi h^2+8\pi^2 mE\psi-8\pi^2 mV\psi=0$

or, $\frac{\nabla^2\psi h^2}{8\pi^2 m}+E\psi-V\psi=0$ or, $\left(-\frac{h^2\nabla^2}{8\pi^2 m}+V\right)\psi=E\psi$ —— (3)

The expression $\left(-\frac{h^2\nabla^2}{8\pi^2 m}+V\right)$ in equation (3) is called Hamiltonian operator denoted by symbol $\hat{H}$. Thus, equation (3) can also be written as $\hat{H}\psi=E\psi$ —— (4)

The Hamiltonian operator ($\hat{H}$) consists of two parts, viz, the kinetic energy part $\left(-\frac{h^2\nabla^2}{8\pi^2 m}\right)$ & the potential energy part (V).

(d) Polar coordinate form:

$$\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\cdot\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\cdot\frac{\partial^2}{\partial\phi^2}\right]\psi+\frac{8\pi^2 mr^2}{h^2}(E-V)\psi=0 \quad \text{——} (5)$$

where r, θ & ϕ are polar coordinates.

⟹ Derivation of Schrodinger's wave equation:

Schrodinger assumed that the electronic waves are similar to stationary waves. He considered an electron wave of amplitude ψ. If x is the displacement of the wave in x direction and λ is its wave length, then ψ is given by

$$\psi=A\sin\frac{2\pi x}{\lambda} \quad \text{——} (1) \quad (\text{where } A = \text{a constant})$$

On differentiating equation (1), we get $\frac{\partial\psi}{\partial x}=\left(A\cos\frac{2\pi x}{\lambda}\right)\cdot\frac{2\pi}{\lambda}=\frac{2\pi A}{\lambda}\cos\frac{2\pi x}{\lambda}$ —— (2)

On differentiating equation (2), we get $\frac{\partial^2\psi}{\partial x^2}=\frac{2\pi A}{\lambda}\left(-\sin\frac{2\pi x}{\lambda}\right)\cdot\frac{2\pi}{\lambda}=-\frac{4\pi^2 A}{\lambda}\sin\frac{2\pi x}{\lambda}$

or, $\frac{\partial^2\psi}{\partial x^2}=-\frac{4\pi^2}{\lambda^2}\psi$ $\left[\because \psi=A\sin\frac{2\pi x}{\lambda}\right]$ —— (3)

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This is the wave equation for unidimensional stationary wave vibrating along x-axis only. When equation (3) is extended to three dimensions, we replace $\frac{\partial^2\psi}{\partial x^2}$ by $\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)$ and hence equation (3) becomes: $\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}=-4\pi^2\psi\times\frac{1}{\lambda^2}$

or, $\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}=-4\pi^2\psi\times\frac{m^2v^2}{h^2}$ —— (4) [from de-Broglie's equation, $\lambda=\frac{h}{mv}$]

Equation (4) is a wave equation which describes the motion of an electron in three dimensions (x, y & z). Now, the total energy (E) of the electron is the sum of its kinetic energy ($\frac{1}{2}mv^2$) and potential energy (V). Thus,

$E=\frac{1}{2}mv^2+V$ or, $\frac{1}{2}mv^2=(E-V)$ or, $v^2=\frac{2(E-V)}{m}$

Substituting the value of v^2 in equation (4), we get

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}=-\frac{4\pi^2\psi m^2}{h^2}\times\frac{2(E-V)}{m}=\frac{8\pi^2m}{h^2}(E-V)\psi$$

$$\therefore \frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2m}{h^2}(E-V)\psi=0 \quad \text{—— (5)}$$

Or, $\nabla^2\psi+\frac{8\pi^2m}{h^2}(E-V)\psi=0$ —— (6) [where $\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$, Laplacian operator]

Equations (5) & (6) are forms of Schrodinger's wave equation.

⇒ Physical Significance or Meaning of ψ & ψ^2:

ψ is wave function and represents the amplitude of wave. From it, almost all physically observable property of a dynamic particle, can be described. It has no 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 value, whereas the probability of finding the electron can be zero or positive but can never be negative.

ψ^2 (square of psi) 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/three dimensions around the nucleus is called electron probability function (D). The value of D for an extremely small spherical shell of radius (r) and thickness (dr) around the nucleus is given by

$D=\psi^2\times$ volume of spherical shell $=4\pi r^2dr.\psi^2$

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

⇒ 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 the 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 $\int|\psi|^2d\tau=1$

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

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