

SCHRODINGER EQUATION FOR HYDROGEN ATOM

The Schrödinger equation of H₂ atom containing one electron & one proton is given by (in spherical polar co-ordinate)

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

Where m = reduced mass of electron & Proton, E is total energy and V = Potential energy.

The three variable r, θ & ϕ are orthogonal to each other.

Let $\psi(r, \theta, \phi) = R(r) Y(\theta) Z(\phi)$ --- (B)

where R_r = function of r only, $Y(\theta)$ = function of θ only and $Z(\phi)$ = function of ϕ only

$$\frac{\partial \psi}{\partial r} = YZ \cdot \frac{\partial R}{\partial r}, \quad \frac{\partial \psi}{\partial \theta} = RZ \cdot \frac{\partial Y}{\partial \theta} \quad \text{and} \quad \frac{\partial^2 \psi}{\partial \phi^2} = RY \frac{\partial^2 Z}{\partial \phi^2}$$

Substituting these value in equation B.

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 YZ \cdot \frac{\partial R}{\partial r} \right] + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left[RZ \frac{\partial Y}{\partial \theta} \right] + \frac{1}{r^2 \sin^2 \theta} RY \frac{\partial^2 Z}{\partial \phi^2} + \frac{2m}{\hbar^2} [E - V] RYZ = 0$$

Multiplying by $r^2 \sin^2 \theta / RYZ$. We get

$$\frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left[r^2 \frac{\partial R}{\partial r} \right] + \frac{\sin \theta}{Y} \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial Y}{\partial \theta} \right] + \frac{1}{Z} \frac{\partial^2 Z}{\partial \phi^2} + \frac{2m}{\hbar^2} [E - V] r^2 \sin^2 \theta = 0$$

$$\frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left[r^2 \frac{dR}{dr} \right] + \frac{\sin \theta}{Y} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right)$$

$$+ \frac{2\mu}{\hbar^2} [E - V] r^2 \sin^2 \theta = -\frac{1}{Z} \frac{\partial^2 Z}{\partial \phi^2} \quad \text{--- (C)}$$

$$\text{Let } -\frac{1}{Z} \frac{\partial^2 Z}{\partial \phi^2} = m^2$$

$$\text{or, } \frac{d^2 Z}{d\phi^2} + m^2 Z = 0 \quad \text{--- (D)}$$

This is the independent equation for ϕ . Now equation (C) may be written as:

$$\frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left[r^2 \frac{dR}{dr} \right] + \frac{\sin \theta}{Y} \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial Y}{\partial \theta} \right]$$

$$+ \frac{2\mu r^2 \sin^2 \theta}{\hbar^2} [E - V] = m^2$$

$$\text{or, } \frac{1}{R} \frac{\partial}{\partial r} \left[r^2 \frac{dR}{dr} \right] + \frac{2\mu r^2}{\hbar^2} [E - V]$$

$$= \frac{m^2}{\sin^2 \theta} - \frac{1}{Y \sin \theta} \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial Y}{\partial \theta} \right] \quad \text{--- (E)}$$

The L.H.S is the function of r only and R.H.S is the function of θ only. They are equal to a constant $l(l+1)$ (let) where l is greater than m .

$$\frac{1}{R} \frac{d}{dr} \left[r^2 \frac{dR}{dr} \right] + \frac{2\mu r^2}{\hbar^2} [E - V] = l(l+1)$$

$$\text{or, } \frac{d^2 R}{dr^2} + \frac{2}{R} \frac{dR}{dr} + \frac{2\mu R}{\hbar^2} [E - V] = \frac{l(l+1)R}{r^2} \quad \text{--- (F)}$$

$$\text{And } \frac{m^2}{\sin^2 \theta} - \frac{1}{Y \sin \theta} \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial Y}{\partial \theta} \right] = l(l+1) \quad (33)$$

$$\text{or, } \frac{m^2}{\sin^2 \theta} - \frac{1}{Y} \left[\frac{\partial^2 Y}{\partial \theta^2} + \cot \theta \frac{\partial Y}{\partial \theta} \right] = l(l+1) \quad (G)$$

The eqn D E & G are independent of ϕ , θ & r .
 The eqn (G) is K/a radial equation. It's solⁿ is given by "associated Laguerre Polynomial function" (P_l^m). This equation may be solved when the energy of bound electron,

$$E_n = - \frac{Z^2 e^4 \mu}{2 \hbar^2 n^2}$$

This is the energy eigen value for H-atom with $Z=1$.

The solution of eqn (G) is given by,

$$Y(\theta) = \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} P_l^m(\cos \theta)$$

where l = azimuthal quantum number. The solⁿ of equation D is given by

$$Z(\phi) = \frac{1}{\sqrt{2\pi}} e^{2m\phi}$$

where m = magnetic quantum number.

These $Y(\theta)$ & $Z(\phi)$ gives the spherical distribution of electron in H₂-atom. So they are called the spherical Eigen function.