*. Separation of Variables:-

The Schrödinger equation in terms of spherical polar co-ordinates may be easily separated into three independent equations, each involving only one co-ordinate. Let us consider the $\psi(r, \theta, \phi)$ can be written as a product of three functions $R(r)$ which depends on r-alone $\Theta(\theta)$ on (θ) alone and $\phi(\varphi)$ on φ alone.

Thus -

$$\psi(r, \theta, \phi) = R(r)\,\Theta(\theta)\,\phi(\varphi) \quad \text{--- (1)}$$

The function $R(r)$ describes how the wave function ψ of the electron varies with the radial distance from the nucleus with ϕ & Θ constant. Similar is the case with $\Theta(\theta)$ & $\phi(\varphi)$.

The equation may be simply written as:

$$\psi = R\,\Theta\,\phi \quad \text{--- (2)}$$

So,

$$\frac{\partial \psi}{\partial r} = \Theta\phi \cdot \frac{\partial R}{\partial r}$$

$$\frac{\partial \psi}{\partial \theta} = R \cdot \phi \cdot \frac{\partial \Theta}{\partial \theta}$$

& $$\frac{\partial \psi}{\partial \phi} = R \cdot \Theta\, \frac{\partial \phi}{\partial \phi}$$

Now putting these values in Schrödinger eqn, we get -

$$\frac{1}{r^2}\left[\Theta\phi\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{R\Theta}{\sin\theta}\cdot\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial \Theta}{\partial \theta}\right) + \frac{R\Theta}{\sin^2\theta}\cdot\frac{\partial^2\phi}{\partial\phi^2}\right]$$

$$+ \frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{4\pi\epsilon_0 \cdot r}\right) r^2\sin^2\theta = 0 \quad \text{--- (3)}$$

On multiplying each term in the eq^n — (3) by $\frac{r^2 \sin^2\theta}{R\Theta\phi}$, we get

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{\sin\theta}{\Theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\cdot\frac{\partial\Theta}{\partial\theta}\right) + \frac{1}{\phi}\frac{\partial^2\phi}{\partial\phi^2}$$

$$+ \frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0 r}\right) r^2\sin^2\theta = 0 \quad \text{— (4)}$$

The 3rd term in the equation — (4) is a function of ϕ only and the other terms are independent of ϕ.

On rearranging eq^n - (4) we get,

$$-\frac{1}{\phi}\cdot\frac{\partial^2\phi}{\partial\phi^2} = \frac{\sin^2\theta}{R}\cdot\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{\sin\theta}{\Theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\cdot\frac{\partial\Theta}{\partial\theta}\right)$$

$$+ \frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0 r}\right) r^2\sin^2\theta \quad \text{— (5)}$$

Let $\quad -\frac{1}{\phi}\cdot\frac{\partial^2\phi}{\partial\phi^2} = m^2 \quad$ — (6)

Then eq^n — (5) be comes

$$\frac{\sin^2\theta}{R}\cdot\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{\sin\theta}{\Theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)$$

$$+ \frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0 r}\right) r^2\sin^2\theta = \frac{1}{m^2}$$

On dividing each term by $\sin^2\theta$ & rearranging, we get

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)r^2 = \frac{m^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\cdot\frac{\partial\Theta}{\partial\theta}\right)$$

This equation envolves one variables in each side and therefore be equal to same constant L. We then have the following two seperate equations —

$$\frac{1}{\sin\theta}\cdot\frac{d}{d\theta}\left(\sin\theta\cdot\frac{d\Theta}{d\theta}\right) + \left(L - \frac{m^2}{\sin^2\theta}\right)\Theta = 0 \quad \text{— (7)}$$

and

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)R - \left(\frac{L}{r^2}\right)R^2 = 0 \quad \text{— (8)}$$

Three variables in the partial differential equation are, thus, seperated into three ordinary differential equations such equation — (6), (7) & (8) to solve.

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