Ans. (a) Schrodinger's equation for *H*-like systems :

Hydrogen-like systems contain two particles, namely, the nucleus and the electron. So, the wave function for such a system depends upon six co-ordinate variables, three for the electron (x_1, y_1, z_1) and three for the nucleus (x_2, y_2, z_2).

The Hamiltonian operator consists of two terms, viz., the kinetic and potential energy terms. The kinetic energy operator will contain two terms, one for the electron and the other for the nucleus. The potential energy of the electron at distance r from the nucleus of charge + Ze (Z = at . no., e = electronic charge) is $-\dfrac{Ze^2}{r}$. Thus, we have

$$\hat{H} = \hat{T} + \hat{V} \quad \begin{bmatrix} \hat{T} = \text{operator for K.E.} \\ \hat{V} = \text{operator for P.E.} \end{bmatrix}$$

$$\text{or,} \quad \hat{H} = \left(-\frac{h^2}{8\pi^2 m}\nabla_1^2 - \frac{h^2}{8\pi^2 M}\nabla_2^2\right) - \frac{Ze^2}{r} \quad - (1)$$

Where m and M are the masses of the electron and the nucleus respectively.

Now, the schrodinger equation for *H*-like systems can be written as

$$\hat{H}\,\psi_T = E_T \psi_T$$

$$\text{or,} \quad \left[\left(-\frac{h^2}{8\pi^2 m}\nabla_1^2 - \frac{h^2}{8\pi^2 M}\nabla_2^2\right) - \frac{Ze^2}{r}\right]\psi_T = E_T \psi_T \quad \dots (2)$$

Where ψ_T is the total wave function and E_T is the total energy of the system.

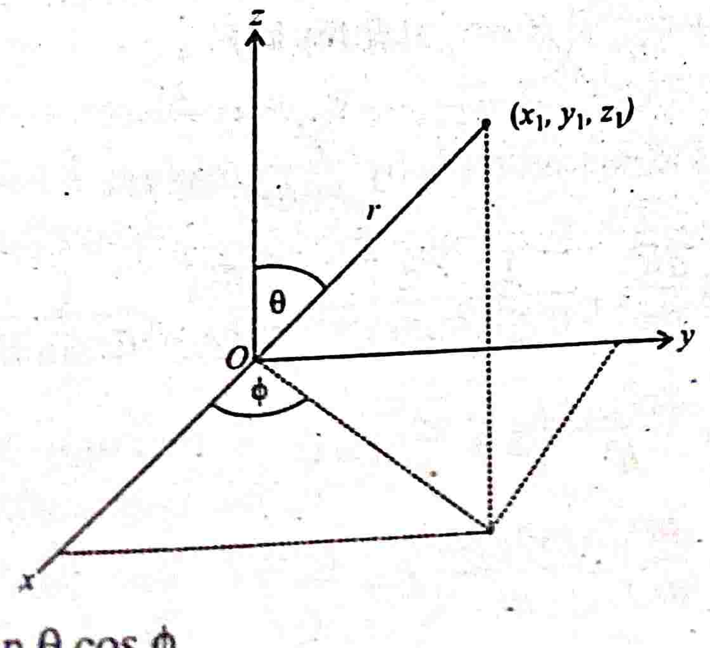
Equation (2) can be separated into two simpler equations, one involving the free movement of the centre of mass of the system in space and the other involving the relative motion of two particles within the system. The two equations are—

$$-\frac{h^2}{8\pi^2 (m + M)} \nabla_2^2 \psi_M = E_{trans.} \cdot \psi_M \qquad \text{... (3)}$$

and $$\left[-\frac{h^2}{8\pi^2\mu} \nabla_1^2 - \frac{Ze^2}{r}\right] \psi = E\psi \qquad \text{... (4)}$$

Equation (3) is actually the schrodinger equation for a free particle of mass $(m + M)$. E_{trans} is the translational kinetic energy associated with the free movement of the centre of mass of the atom through space. Equation (4) is the schrodinger equation which represents the system in which an electron of reduced mass μ is revolving around the stationary nucleus of charge $+ Ze$ at a distance of r. The behaviour of this electron can be described by the wave function ψ and E, the corresponding energy of the electron. The latter equation is relevant here for consideration.

In the present case, the potential energy field is spherical (V depends only upon r), and hence it is convenient to transform the cartesian co-ordinates, $(x_1, y_1\ z_1)$ into the spherical polar co-ordinates r, θ and ϕ by using the relations.



$$x_1 = r \sin\theta \cos\phi$$

$$y_1 = r \sin\theta \sin\phi, \text{ and}$$

$z_1 = r\cos\theta.$

Here, r = radial distance of the electron (x_1, y_1, z_1) from the nucleus. (0 to ∞)

θ = Zenith angle (0 to π)

ϕ = Azimuthal angle (0 to 2π)

Transforming the cartesian co-ordinates into spherical polar co-ordinates, the schrodinger equation (4) can be written as

$$\frac{1}{r^2}\left\{\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}\psi(r,\theta,\phi)$$

$$+\frac{8\pi^2\mu}{h^2}\left(E+\frac{Ze^2}{r}\right)\psi(r,\theta,\phi)=0 \qquad \text{... (5)}$$

Here, $\psi(r, \theta, \phi)$ is the function of polar co-ordinates r, θ, and ϕ.

(b) **Separation of variables r, θ and ϕ :** The function $\psi(r, \theta, \phi)$ may be written as the product of three functions $R(r)$, $\Theta(\theta)$ and $\Phi(\phi)$ which are functions of r, θ and ϕ only respectively, i.e.,

$$\psi(r,\theta,\phi) = R(r).\,\Theta(\theta)\,\Phi(\phi) \qquad \text{... (6)}$$

Putting the value of $\psi(r, \theta, \phi)$ from equation (6) in equation (5), we get

$$\frac{1}{r^2}\left[\Theta\Phi\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{R\Phi}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{R\Theta}{\sin^2\theta}\frac{d^2\Phi}{d\phi^2}\right]$$

$$+\frac{8\pi^2\mu}{h^2}\left(E+\frac{Ze^2}{r}\right)R\Theta\Phi=0 \qquad \text{...(7)}$$

Multiplying the equation (7) by $\frac{r^2}{R\Theta\Phi}$, we get

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

$$+\frac{8\pi^2\mu r^2}{h^2}\left(E+\frac{Ze^2}{r}\right)=0$$

$$\text{or,}\quad \frac{1}{R}\cdot\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{8\pi^2\mu r^2}{h^2}\left(E+\frac{Ze^2}{r}\right)$$

$$=-\frac{1}{\Theta\sin\theta}\cdot\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)-\frac{1}{\Phi\sin^2\theta}\frac{d^2\Phi}{d\phi^2} \qquad \text{... (8)}$$

The equation (8) holds good only when both sides are equal to a constant, say, $l\,(l + 1)$. Thus, the equation (8) separates into two equations, one depending only on r and the other on θ and ϕ. These are :

(i) The radial equation :

$$\frac{1}{R} \cdot \frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{8\pi^2 \mu r^2}{h^2}\left(E + \frac{Ze^2}{r}\right) = l\,(l + 1) \qquad \dots (9)$$

(ii) The angular equation :

$$\frac{1}{\theta \sin \theta} \cdot \frac{d}{d\theta}\left(\sin \theta \frac{d\theta}{d\theta}\right) + \frac{1}{\Phi \sin^2\theta} \frac{d^2\Phi}{d\phi^2} = -\, l\,(l + 1) \qquad \dots(10)$$

Now the angular equation (10) can be further separated into two equations, one depending only on θ and the other on ϕ. Multiplying equation (10) with $\sin^2\theta$ and rearranging, we get

$$\frac{\sin \theta}{\theta} \cdot \frac{d}{d\theta}\left(\sin \theta \,.\, \frac{d\theta}{d\theta}\right) + l\,(l + 1) \sin^2\theta = -\frac{1}{\Phi} \frac{d^2\Phi}{d\varphi^2} \qquad \dots (11)$$

The two sides of the equation (11), must be equal to a constant, say, m^2. Thus, we have

$$\frac{\sin \theta}{\theta} \cdot \frac{d}{d\theta}\left(\sin \theta \frac{d\theta}{d\theta}\right) + l\,(l + 1) \sin^2\theta = m^2 \qquad \dots(12)$$

and,
$$\frac{1}{\Phi} \cdot \frac{d^2\Phi}{d\varphi^2} = -\, m^2 \qquad \dots (13)$$