SCHROEDINGER EQUATION IN SPHERICAL POLAR COORDINATES

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\csc\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\csc^2\theta\frac{\partial^2}{\partial\phi^2}\right]\psi(r,\theta,\phi)+U(r,\theta,\phi)\,\psi(r,\theta,\phi)=E\,\psi(r,\theta,\phi) \qquad (6\text{–}10)$$

Separate variables: 1. Assume $\psi(r,\theta,\phi) = R(r)\,\Theta(\theta)\,\Phi(\phi)$ 2. Insert and divide by $R(r)\,\Theta(\theta)\,\Phi(\phi)$

ϕ–PART

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{1}{\Theta}\csc\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\csc^2\theta\left(\underbrace{\left\{\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}\right\}}_{\phi-\text{separate}}\right)=-r^2\frac{2m\left(E-U(r)\right)}{\hbar^2} \qquad (6\text{–}11)$$

$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = \text{constant} \Rightarrow \begin{cases}\text{exponential if constant}>0\\ \text{sinusoidal if constant}<0\end{cases}$. But because Φ *must meet itself smoothly* at $\phi = 0$ and $\phi = 2\pi$, Φ must be periodic/sinusoidal, and the constant must be the negative of the square of an integer. Call it $-m_\ell^2$ [**quantum number 1**]

θ–PART

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\underbrace{\left\{\frac{1}{\Theta}\csc\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\csc^2\theta\,(-m_\ell^2)\right\}}_{\theta-\text{separate}}=-r^2\frac{2m\left(E-U(r)\right)}{\hbar^2} \qquad (6\text{–}12)$$

$$\csc\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right)-m_\ell^2\csc^2\theta\,\Theta(\theta)=C_\theta\,\Theta(\theta) \qquad (6\text{–}17a)$$

$\Theta(\theta)$ *diverges* unless $C_\theta = 0, -2, -6, -12, \ldots = -\ell(\ell+1)$ [**quantum number 2**] and unless $m_\ell \leq \ell$.

r–PART

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\ell(\ell+1)=-r^2\frac{2m\left(E-U(r)\right)}{\hbar^2} \qquad (6\text{–}24)$$

Assuming hydrogen–atom $U(r) = -\frac{1}{4\pi\epsilon_o}\frac{e^2}{r}$ (i.e., electron–proton potential energy),

$R(r)$ *diverges* unless $E = -\frac{m\,e^4}{2(4\pi\epsilon_o)^2\hbar^2}\frac{1}{n^2}$ [**quantum number 3**] and $\ell < n$