Quantum theory for hydrogen atom

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- Assume that: proton is stationary
- symmetry suggests polar coordinates.
- For one electron in three dimensions,

$$\underbrace{\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}}_{\nabla^2 \psi} + \frac{2m}{\hbar^2}(E-U)\psi = 0 \quad \text{—(1)}$$

where E = total energy, $U = P.E. = \left(\frac{-e^2}{4\pi\epsilon_0 r}\right)$.

- lets convert to (r, θ, ϕ), θ = zenith angle $\in [0, \pi]$
  ϕ = azimuth angle $\in [0, 2\pi)$

$$\Rightarrow \sin^2\theta \frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) + \sin\theta \frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \psi}{\partial \theta}\right) + \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2mr^2 \sin^2\theta}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r^2} + E\right)\psi = 0 \quad \text{—(2)}$$

- We take here:
  (a) ψ → Normalisable
  (b) ψ and its derivatives are continuous and single-valued functions.

\# Solving the eqn. (2), will give three set of quantum numbers.

To define a particle's motion in three-dimensional box, we need three quantum numbers.
[Bohr only considers one quantum model].

(because ψ must be zero at the walls of the box in the x, y, z-directions.)

** and in hydrogen atom, electron's motion is guided by inverse square electric field of the nucleus and not by the walls.

Seperation of variables :-

$$\Rightarrow \psi(r,\theta,\phi) = R(r)\cdot\Theta(\theta)\cdot\Phi(\phi)$$

only depend on r — only on θ — only on ϕ.

- Substitute the values in eq^n: ② :

$$\Rightarrow \frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} + \frac{2mr^2\sin^2\theta}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} + E\right) = 0.$$

$$\Rightarrow \frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) = \lambda \text{ (say)},$$

hence $\Rightarrow$ $$\boxed{\lambda + \frac{2mr^2\sin^2\theta}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} + E\right) = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}} \quad ③$$

This equation can be correct only if both sides of it are equal to the same constant, since they are functions of different variables,

$$\boxed{-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = m_l^2} \quad ④$$

$$\Rightarrow \frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{2mr^2\sin^2\theta}{\hbar^2}(\dots) = m_l^2.$$

$\Rightarrow$ Divide by $\sin^2\theta$:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2mr^2}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} + E\right) = m_l^2 - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)$$

Again same thing, both should be equal to some common constant, here, that constant is $l(l+1)$.

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$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{2m}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r}+E\right)-\frac{l(l+1)}{r^2}\right]R=0. \quad (5)$$

and

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d(\theta)}{d\theta}\right)+\left(l(l+1)-\frac{m_l^2}{\sin^2\theta}\right)\Theta=0 \quad (6)$$

$\boxed{4,5,6}$ gives the respective separation of variable equations.