CH107 — T4 3

① $\psi(\theta) = Ae^{ik\theta} + Be^{-ik\theta}$

$= C\cos k\theta + D\sin k\theta$

$\frac{d\psi}{d\theta} = iAke^{ik\theta} - Bike^{-i\theta}$

$\frac{d^2\psi}{d\theta^2} = -Ak^2e^{i\theta k} - Bk^2e^{-ik\theta}$

$= -k^2 (Ae^{ik\theta} + Be^{-ik\theta})$

$= [-k^2] \psi(\theta)$

$\therefore \frac{-\hbar^2}{2I} \frac{d^2\psi}{d\theta^2} = \underline{\underline{\left(\frac{\hbar^2k^2}{2I}\right)}} \cdot \underline{\psi(\theta)}$

Boundary condition

$\psi(\theta) = \psi(2\pi + \theta)$

$Ae^{ik\theta} + Be^{-ik\theta} = Ae^{ik\theta} \cdot e^{ik2\pi} + Be^{-ik\theta} \cdot e^{-ik\pi}$

$Ae^{ik\theta} \underbrace{(1 - e^{ik2\pi})} + Be^{-ik\theta} \underbrace{(1 - e^{-ik2\pi})} = 0$

$e^{i(2\pi k)} = 1$

$\hookrightarrow \boxed{k \in \mathbb{Z}}$

Ans ⓐ Acceptable sol^n → $\psi = Ae^{ik\theta} + Be^{-ik\theta}$

ⓑ $E_n = \frac{n^2\hbar^2}{2I}$ (k in our derivat^n)

ⓒ $n \in \mathbb{Z} = 0, \pm1, \pm2 - - - -$

② $Y_1^0 = A\cos\theta$ ⟶ $0 \le \theta \le \pi$

Normalization ⟶ $\int_0^{2\pi}\int_0^{\pi} |A^2 Y_1^0|^2 \sin\theta \, d\theta \, d\phi = 1$

$$A^2 \int_0^{\pi} \cos^2\theta = 1$$

$$2A^2 \int_0^{\pi/2} \cos^2\theta = 1 \longrightarrow ①$$

$$2A^2 \int_0^{\pi/2} \sin^2\theta = 1 \longrightarrow ②$$

$$2A^2 \int_0^{\pi/2} 1 \, d\theta = 1$$

$$\cancel{2}A^2 \cdot \frac{\pi}{\cancel{2}} = 1$$

$$A = \frac{1}{\sqrt{\pi}}$$

$$\int_0^{2\pi}\left(\int_0^{\pi} A^2\cos^2\theta \sin\theta \, d\theta\right) d\phi = 1$$

$$A^2 \cdot \frac{2}{3} \times 2\pi = 1$$

$$A = \sqrt{\frac{3}{4\pi}}$$

we're including Φ as we are solving rigid rotor

$[Y_{lm}^0(\theta, \phi)]$ ☆

③ $Y_1^0 = \frac{1}{\sqrt{\pi}} \cos\theta$

$$L^2 Y_1^0 = \frac{-\hbar^2}{\sqrt{\pi}}\left[\frac{1}{\sin\theta}\left[\frac{\partial}{\partial\theta}\left\{(\sin\theta)\cdot\frac{\partial}{\partial\theta}\cos\theta\right\}\right]\right] + \frac{1}{\pi\sin^2\theta}\frac{\partial^2 Y_1^0}{\partial^2\phi}$$

$$\frac{-\hbar^2}{\sqrt{\pi}} \cdot \frac{1}{\sin\theta}\left[\frac{-\partial}{\partial\theta}\sin^2\theta\right]$$

$$+\frac{\hbar^2}{\sqrt{\pi}} \frac{1}{\sin\theta} + 2\sin\theta\cos\theta$$

$$L^2 Y_1^0 = \frac{2\hbar^2}{\sqrt{\pi}} \cos\theta$$

$$L^2 Y_1^0 = 2\hbar^2 Y_1^0 \longrightarrow \hat{O}\psi = E\psi$$

ψ is eigenfn of L^2

Eigen value $= 2\hbar^2$.

4(a) In cartesian coordinates TISE of electronic part takes the following form:-

$$\left[\frac{-\hbar^2}{2\mu} \nabla_r^2 - \frac{Ze^2}{\sqrt{x^2+y^2+z^2}} \right] \psi_e = E\psi_e$$

Due to the term $\sqrt{x^2+y^2+z^2}$, the equation can't be solved by seperating variable and the mathematical treatement becomes complicated.

Whereas if spherical polar coordinates are used $\psi(R,\theta,\phi)$ can be convinently separated as $R(r) \cdot \Theta(\theta)\, \Phi(\phi)$ which enables us to solve TISE easily. Hence it is necessary to use spherical polar coordinates.

(b) For hydrogen atom

$$\psi(R,\theta,\phi) = R_{n,l}(r) \cdot \Theta_{l,m}(\theta)\, \Phi_m(\phi)$$

In case of rigid rotor, we have r (fixed) $= R$ (say) in that case $R(r)$ is technically a constant ~~which~~ & the equation can be re written as

$$\psi(\theta,\phi) = \Theta_{l,m}(\theta)\, \Phi_m(\phi)$$

which are dependent on 2 QNs than 3.

$$\nabla^2_{r,\theta,\phi} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \quad -(1)$$

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \quad (2)$$

using (2)

$$\nabla^2_{r,\theta,\phi} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$$= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2} \times \frac{-L^2}{\hbar^2}$$

$$= \frac{1}{r^2}\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\hat{L}^2}{\hbar^2}\right)$$