3D QM

$$H|E\rangle = E|E\rangle$$ ⇐ Eigenvalue Problem

$$H_{cm}|E_{cm}\rangle = E_{cm}|E_{cm}\rangle$$ ⇐ Free Particle

$$H_{rel}|E_{rel}\rangle = E_{rel}|E_{rel}\rangle$$ ⇐ Bound States

Hydrogen

$$H \equiv H_{rel} \doteq \frac{|\vec{P}_{rel}|^2}{2\mu} + V(r)$$ ⇐ Move to spherical coords b/c $V(r)$

spherically sym.

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

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{\hbar^2 r^2}L^2\right]\psi(r,\theta,\phi)$$

$$+V(r)\,\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

3D PDE → tough to solve

Separable Solution

(481 Laplace's Eqn
$\nabla^2 V = 0$
$V = X(x)Y(y)Z(z)$)

$$\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)$$

proposed solution r from θ & ϕ

$\Rightarrow$ θ from ϕ as well

$Y \frac{d}{dr}(R) \quad R \frac{d}{d\theta} \quad \frac{d}{d\phi} \quad Y$

$$-\frac{\hbar^2}{2m}\left[Y \frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) - \frac{1}{\hbar^2 r} R L^2 Y\right]$$

$$+V(r)RY = ERY$$

isolate r dependence from everythings else

Dividing by ψ. $\psi \neq 0$

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{R}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{1}{Y}\frac{1}{\hbar^2 r^2}L^2Y\right]$$

$$+V(r) = E$$

multiply by r^2

$$-\frac{\hbar^2}{2\mu}\left[\underbrace{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)}-\underbrace{\frac{1}{Y}\frac{1}{\hbar^2}L^2Y}\right]+\underbrace{V(r)r^2}$$

group by r & θ,ϕ $= Er^2$

only function of r

$$\overbrace{\frac{1}{R}\left(\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)\right)+\frac{2\mu}{\hbar^2}\left(E-V(r)\right)r^2}$$

?

$$= \underbrace{\frac{1}{\hbar^2}\frac{1}{Y}L^2Y}$$

only function of θ,ϕ

$$\boxed{f(r) = g(\theta,\phi)}$$ for all r,θ,ϕ

change $r\uparrow\downarrow$ = don't have to change θ,ϕ

$f(r) = A = g(\theta, \phi)$ Key steps

separation constant in Sep. Var.

$$\boxed{\begin{gathered} L^2 Y(\theta,\phi) = A\hbar^2 Y(\theta,\phi) \quad (1) \\ \left(\frac{-\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + V(r) + A\frac{\hbar^2}{2mr^2}\right)R(r) = ER(r) \quad (2) \end{gathered}}$$

$\psi = RY$

Eqn 1 → this week & next

Eqn 2 → March 15

↳ Hydrogen Atom

$$\underline{L}^2 Y(\theta,\phi) = \underline{A}\hbar^2 \boxed{Y(\theta,\phi)} \rightarrow |l m_l\rangle \doteq Y(\theta,\phi)$$

position rep.

$$\boxed{L^2 \underline{|l m_l\rangle} = \underline{l(l+1)}\hbar^2 |l m_l\rangle}$$

$$A = \underline{l(l+1)}$$

Sep of Var part 2

$$L^2 Y(\theta,\phi) = A\hbar^2 Y(\theta,\phi)$$

$$Y(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$$ proposed separable soln.

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

① pop in proposed soln.

$$-\cancel{\hbar^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\Theta\,\Phi = A\cancel{\hbar^2}\,\Theta\,\Phi$$

② let operators act

$$-\Phi\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{d\Theta}{d\theta}\right) + \Theta\frac{1}{\sin^2\theta}\frac{\partial^2\Phi}{d\phi^2} = A\,\Theta\,\Phi$$

③ Divide by $\frac{4}{}$ ($Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$)

$$-\frac{1}{\Theta}\left(\frac{1}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{1}{\Phi}\frac{1}{\sin^2\theta}\frac{d^2\Phi}{d\phi^2} = A$$

④ Get rid of additional dep. ($\sin^2\theta$)

$$-\frac{1}{\Theta}\left(\sin\theta\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = A\sin^2\theta$$

⑤ Isolate θ, ϕ

$$\underbrace{-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}}_{\text{function of } \phi \text{ only}} = \underbrace{A\sin^2\theta + \frac{1}{\Theta}\left(\sin\theta\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta}\right)}_{\text{function of } \theta \text{ only}}$$

$$f(\phi) = g(\theta) = B$$ ← new sep. constant.

$$③ \quad \frac{d^2\Phi}{d\phi^2} = B\Phi$$

$$④ \quad \frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{B}{\sin^2\theta}\Theta(\theta) = -A\Theta(\theta)$$

Eqn 1 → $R(r)$

Eqn 2 → $Y(\theta,\phi)$

Eqn 3 $\Phi(\phi)$ ⟸ Wednesday last week

Eqn 4 $\Theta(\theta)$

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

Sep. of Variables

3D problem → 3D PDE

↪ 3 1D ODE's

⇓

adding 2 separation consts. unknown.

ND problem → ND PDE

↪ N 1D ODE's

⇓

N-1 separation constants.

① Actual 1D problem - $\Phi(\phi)$

② 2D problem θ, ϕ be used $Y(\theta, \phi)$

3 3D problem solve $R(r)$