1D → 3D

TDSE $\quad i\hbar \frac{\partial \Psi(\text{space},t)}{\partial t} = \hat{H}\, \Psi(\text{space},t)$

$\hat{H} = \frac{\hat{p}^2}{2m} + V(\text{space})$

For x, y, z : $\quad \frac{\hat{p}^2}{2m} \rightarrow \frac{(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2)}{2m}$ where $\hat{p}_i = -i\hbar \frac{\partial}{\partial x_i}$

comes from $\langle \vec{p} \rangle = \frac{d\langle \vec{x} \rangle}{dt}$

$\hat{p} = -i\hbar \hat{\nabla} \quad \Rightarrow$ TDSE $\boxed{i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi}$

∇^2 depends on coordinate choice.

Nature loves r, θ, ϕ :

$$\nabla^2_{r\theta\phi} = \underbrace{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\left(\frac{\partial^2}{\partial \phi^2}\right)}_{\text{necessary evil for hydrogen!}}$$

Normalization: $\int \underbrace{|\Psi|^2}_{m^{-3}} dV = 1$

TDSE $\quad i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$

Start with an expansion in separable states: $\Psi = \sum_n c_n \underbrace{\psi_n(\text{space}, t)}$

$\phi_n(t)\,\psi_n(\text{space})$

$$i\hbar \frac{\partial \phi_n(t)}{\partial t}\psi_n(\text{space}) = \hat{H}\phi_n(t)\psi_n(\text{space})$$

assume $\hat{H}(\hat{x}, \hat{p})$ w/out t

or

$$\underbrace{i\hbar \frac{\partial \phi_n(t)}{\partial t}\frac{1}{\phi_n(t)}}_{\text{only on } t} = E_n = \underbrace{\frac{1}{\psi_n(\text{space})}\hat{H}\psi_n(\text{space})}_{\text{only on space}}$$

$$\Downarrow \qquad\qquad\qquad \Downarrow$$

$$\phi_n(t) = e^{-i\frac{E_n}{\hbar}t} \qquad\qquad \hat{H}\psi_n(\text{space}) = E_n\,\psi_n(\text{space}) \quad \text{TISE}$$

Central Potentials $V(r)$

Assume: $\Psi_{(space)} = R(r)\,\Theta(\theta)\,\Phi(\phi)$

$$\left\{-\frac{\hbar^2}{2m}\left[\Theta\Phi\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + R\Phi\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{R\Theta}{r^2\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}\right] + VR\Theta\Phi - ER\Theta\Phi = 0\right\} \times \frac{2mr^2}{\hbar^2}\frac{1}{R\Theta\Phi}$$

$$\underbrace{\left[\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2mr^2}{\hbar^2}(V(r)-E)\right]}_{\text{only "r"}} + \underbrace{\left[\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)\right] + \left[\frac{1}{\Phi}\frac{1}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}\right]}_{\text{no "r"}} = 0$$

$= \ell(\ell+1)$ $\qquad\qquad$ $= -\ell(\ell+1)$

any complex constant

I. Radial eqn: $\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2mr^2}{\hbar^2}(V(r)-E) = \ell(\ell+1)$

II. Angular eqn: $\underbrace{\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \sin^2\theta\,\ell(\ell+1)}_{\text{only "}\theta\text{"}} + \underbrace{\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}}_{\text{only "}\phi\text{"}} = 0$

$= m^2$ $\qquad\qquad$ $= -m^2$

any complex constant

"azimuthal"

IIa. "Magnetic" equation: $\frac{\partial^2\Phi}{\partial\phi^2} = -m^2\Phi \Rightarrow \Phi = e^{im\phi}$ $\quad m = 0, \pm1, \pm2 \dots$ for $\Phi(2\pi) = \Phi(0)$

IIb. "Polar" eqn:

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \left[\sin^2\theta\,\ell(\ell+1) - m^2\right]\Theta = 0$$

$$\Theta(\theta) = \underbrace{A(1-\cos^2\theta)^{|m|/2}\left(\frac{d}{d\cos\theta}\right)^{|m|}\left[\underbrace{\frac{1}{2^\ell \ell!}\left(\frac{d}{d\cos\theta}\right)^\ell(\cos^2\theta-1)^\ell}_{P_\ell(\cos\theta)\ \text{Legendre polynomial of degree } \ell}\right]}_{P_\ell^m(\cos\theta)\ \text{associated Legendre function}}$$

Note: a) $\frac{\partial^2\Phi}{\partial\phi^2} = k\Phi \Rightarrow \Phi = e^{\sqrt{k}\,\phi}$ but we need $\Phi(0) = \Phi(2\pi)$

$1 = e^{\sqrt{k}\,2\pi}$

$\Downarrow$

$\sqrt{k} = \pm n i$

$k = -n^2$

b) $\ell \geq 0$ for $\left(\frac{d}{d\cos\theta}\right)^\ell$ to make sense

c) If $|m| > \ell$ then $P_\ell^m(\cos\theta) = 0$

d) Constraint on m from ℓ comes from S.O.V.

Collect results: $Y(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$

Normalize: $\underset{\text{const}}{\int |\Psi|^2 r^2\sin\theta\, dr\, d\theta\, d\phi} = \underbrace{\int |R|^2 r^2 dr}_{=1} \underbrace{\int |Y|^2 \sin\theta\, d\theta\, d\phi}_{=1} = 1$

$$Y_\ell^m(\theta,\phi) = \epsilon\sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}}\; e^{im\phi} P_\ell^m(\cos\theta)$$

Spherical Harmonics

$$\int (Y_\ell^m)^* Y_{\ell'}^{m'} \sin\theta\, d\theta\, d\phi = \delta_{\ell\ell'}\delta_{mm'}$$

No Surprise!

Radial Equation

Tidy by $u(r) \equiv r R(r)$

Then: $$-\frac{\hbar^2}{2m}\frac{\partial^2 u}{\partial r^2} + \underbrace{\left[V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]}_{\text{V_{eff} differs from $V(r)$ for $\ell \neq 0$}} u = E u$$

$$V(r) = \begin{cases} \infty\text{-well} & 0 \quad r \leq a \\ & \infty \quad r > a \\ \text{finite-well} & -V_0 \quad r \leq a \\ & 0 \quad r > 0 \\ \text{coulomb} & -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \quad \text{(hydrogen)} \end{cases}$$

Degeneracy: E will not depend on m, so different P_ℓ^m, $P_\ell^{m'}$ will have same energy (degenerate)!!