QM in 3D

$$\boxed{i\hbar \frac{\partial \Psi}{\partial t} = H\Psi}$$

$$H = \frac{p^2}{2m} + V = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + V(x,y,z)$$

$$\left.\begin{array}{l} p_x = \frac{\hbar}{i}\frac{\partial}{\partial x} \\ \quad y \qquad\quad y \\ \quad z \qquad\quad z \end{array}\right\} \quad \boxed{\vec{p} = \frac{\hbar}{i}\vec{\nabla}}$$

$$\boxed{i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi}$$

$$\underline{\text{Laplacian}} \quad \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

prob. dens. $|\Psi(x,y,z,t)|^2$

prob. to find particle in infinitesimal volume in time $\underline{t}$

$$|\Psi(x,y,z,t)|^2\, dx\, dy\, dz = |\Psi(\vec{r},t)|^2\, d^3\vec{r}$$

$$\int |\Psi(\vec{r},t)|^2\, d^3\vec{r} = 1$$

if potential is indep. of time

$V(x,y,z,\cancel{t})$

stationary states

$\hookrightarrow \Psi_n(\vec{r},t) = \psi_n(\vec{r})\, e^{-iE_nt/\hbar}$

time-indep. Schröd. eq.

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi}$$

$$\Psi(\vec{r},t) = \sum c_n \psi_n(\vec{r})\, e^{-iE_nt/\hbar}$$

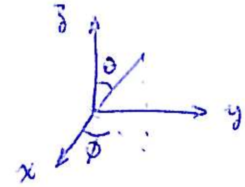
$\longrightarrow \quad [x, p_x] = \hbar i \qquad [x, p_y] = 0$

Summary - overview

→) $V(r)$: potential depends only on the distance from the origin (classical mech. → central forces)

} Coulomb $\boxed{const/r}$ gravitational $\boxed{const/r}$

<u>spherical coordinates</u>: $x = r \sin\theta \cos\phi$
$y = r \sin\theta \sin\phi$
$z = r \cos\theta$



<u>time-indep.</u> Schröd. eq.

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi + V \Psi = E \Psi \Rightarrow \quad (\text{Eq. } 4.14)$$

↓

strategy to solve it

→) separation of variables: $\Psi(r,\theta,\phi) = R(r)\, Y(\theta,\phi) = R(r)\, \Theta(\theta)\, \Phi(\phi)$

↓

every step has a constant associated with it

<u>before</u>

•) position vs. time ⇒ $\boxed{E}$ was the const

($\boxed{\text{energy}}$ is conserved)

each conserved quantity has a quantum number associated with it

E (quantized) → (n) → $\boxed{\text{principal quantum number}}$

<u>now</u>

•) r vs. angles ⇒ $\boxed{l(l+1)}$ is the const

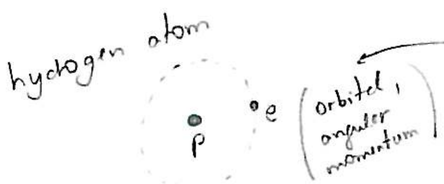
l associated with cons. of total $\boxed{\text{angular momentum}}$

azimuthal quantum number

•) Θ vs ϕ ⇒ $\boxed{m^2}$ is the const.

m associated with cons. of $\boxed{\text{angular momentum in } z}$

(m → orientation of the orbital) magnetic quantum number



(l → shape of the orbital)

→) 3 equations to solve

- $\Phi(\phi) \rightarrow m \longrightarrow$ easy $\rightarrow \Phi(\phi) = e^{im\phi}$

put m into next eq which now deps. on ℓ

- $\Theta(\theta) \rightarrow \ell \longrightarrow P_\ell^m(\cos\theta)$ } associated Legendre function

$Y_\ell^m(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$

$Y_\ell^m(\theta,\phi) = (\text{Norm})\, e^{im\phi}\, P_\ell^m(\cos\theta)$

SPHERICAL HARMONICS

- $R(r) \rightarrow n$ (E: energy) $\longrightarrow$ solution depends on the potential $V(r)$
  - infinite spherical well
  - hydrogen atom / Coulomb $\frac{\text{const}}{r}$

→) Hydrogen atom

$$\boxed{E_n = \frac{E_1}{n^2}}$$

$n = 1, 2, 3 \ldots$

$E_1 = -13.6$ eV (ground state energy)

$$E_1 = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]$$

mass, charge, permittivity of space

$E_1 = -13.6$ eV (binding energy)

$E_2 = -3.4$ eV

↳ easier to ionize the atom

associated Laguerre polynomial

$$\boxed{\psi_{n\ell m} = \left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}\, e^{-r/na}\left(\frac{2r}{na}\right)^\ell \left[L_{n-\ell-1}^{2\ell+1}(2r/na)\right] Y_\ell^m(\theta,\phi)}$$

→ orthogonal since Y_ℓ^m are orthogonal

$$\boxed{a \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2}} = 0.529 \times 10^{-10}\,\text{m}$$

→ most probable position of the electron in the ground state

↳ Bohr radius

(spherical harmonics)

→) algebraic method for $Y_\ell^m(\theta, \phi)$

idea is to look at angular momentum $\vec{L} = \vec{r} \times \vec{p}$

- L_x, L_y, L_z → DO NOT commute

  ⇓

  CAN NOT know all 3 directions

  don't share same eigenfunctions

- L_x, L_y, L_z commute with square of the total angular momentum

  $$L^2 \equiv L_x^2 + L_y^2 + L_z^2$$

L^2 and L_i share the same eigenfunctions

spherical harmonics Y_ℓ^m are eigenfunctions of L_z and L^2

$$\boxed{L^2 Y_\ell^m = \hbar^2 \ell(\ell+1) Y_\ell^m} \quad \text{and} \quad \boxed{L_z Y_\ell^m = \hbar m Y_\ell^m}$$

use ladder operators

$$L_\pm \equiv L_x \pm i L_y$$

→) H, L^2, L_z commute, are compatible observables, have the same eigenfunctions

$$H\psi = E\psi \qquad L^2\psi = \hbar^2 \ell(\ell+1)\psi \qquad L_z\psi = \hbar m \psi$$

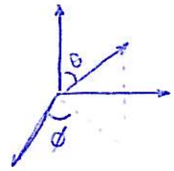
HW: 4.2, 4.3, 4.13(a), 4.18, 4.19

Spherical coordinates

$z = r\cos\theta$

$x = r\sin\theta\cos\phi$

$y = r\sin\theta\sin\phi$



$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi} \leftarrow \text{time indep. Schröd. eq.}$$

$$\psi(r,\theta,\phi)$$

partial   partial

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\psi\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\phi^2}\right)\right] + V\psi = E\psi$$

◦) $V(r) \leftarrow$ only r

◦) look for solutions that are separable

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

ordinary   partial

$$-\frac{\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] + V(r)RY = ERY$$

$$\times\frac{1}{RY}\times\left(-\frac{2mr^2}{\hbar^2}\right)$$

$$\underbrace{\left\{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\left[V(r)-E\right]\right\}}_{\boxed{l(l+1)}\ \text{const}} + \underbrace{\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{\partial^2 Y}{\partial\phi^2}\right\}}_{\boxed{-l(l+1)}\ \text{const}} = 0$$

radial equation   angular equation

Angular Equation

$\times \left(Y \sin^2\theta \right)$

$$\Rightarrow \quad \sin\theta \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial Y}{\partial\theta}\right) + \frac{\partial^2 Y}{\partial\phi^2} = -l(l+1)\sin^2\theta \, Y$$

separation of variables

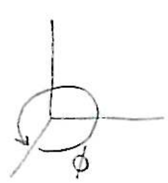
$$Y(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$$

$\times \frac{1}{\Theta\Phi}$

$$\Rightarrow \underbrace{\frac{1}{\Theta}\left[\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right)\right] + l(l+1)\sin^2\theta}_{m^2} + \underbrace{\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}}_{-m^2} = 0$$

•) $\frac{d^2\Phi}{d\phi^2} = -m^2\Phi \Rightarrow \boxed{\Phi(\phi) = e^{im\phi}}$ m ⊕ and ⊖

const absorbed in Θ



after 2π back to the same point

$$\Rightarrow \Phi(\phi + 2\pi) = \Phi(\phi)$$

$$\Rightarrow e^{im2\pi} = 1 \Rightarrow \underline{m = 0, \pm 1, \pm 2, \ldots}$$

c) The θ equation

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

$$\boxed{\Theta(\theta) = A\, P_\ell^m(\cos\theta)}$$

$\hookrightarrow$ associated Legendre function

$$P_\ell^m(x) \equiv (1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|} \underbrace{P_\ell(x)}$$

$\hookrightarrow$ Legendre polynomial

$$P_\ell(x) \equiv \frac{1}{2^\ell \ell!}\left(\frac{d}{dx}\right)^\ell (x^2-1)^\ell$$

$\Rightarrow$ $\ell \geq 0$ because there is no factorial of $-\ell$

Exs: $P_0(x) = 1$

$P_1(x) = \frac{1}{2}\frac{d}{dx}(x^2-1) = x$

$\vdots$

$|m| < \ell$ (if $|m| > \ell \Rightarrow P_\ell^m = 0$ because P_ℓ is a polynomial of degree ℓ)

therefore:

$$\boxed{\Theta(\theta) = A\, P_\ell^m(\cos\theta)}$$

with $\boxed{\ell \geq 0}$ integer (azimuthal quantum number) and $\boxed{|m| < \ell}$ (magnetic quantum number)

$\hookrightarrow$ $m = \underbrace{-\ell, -\ell+1, \ldots, -1, 0, +1, \ldots \ell-1, \ell}_{(2\ell+1)\text{ values}}$

Normalization

$$\int |\psi|^2 \, d^3\vec{r} = \iiint |\psi|^2 r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$= \underbrace{\int_0^\infty |R|^2 r^2 \, dr}_{1} \; \underbrace{\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta \, |Y|^2}_{1} = 1$$

it is convenient to normalize radial and angular parts separately

Normalized angular wave function $\rightarrow$ SPHERICAL HARMONICS

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

$$\begin{cases} \epsilon = (-1)^m & \text{for } m \geq 0 \\ \epsilon = 1 & \text{for } m \leq 0 \end{cases}$$

they are orthogonal

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta \, \left(Y_\ell^m\right)^* \left(Y_{\ell'}^{m'}\right) = \delta_{\ell\ell'} \delta_{mm'}$$

Prob. 4.3 ([illegible])

$$Y_0^0 = (-1)^0 \sqrt{\frac{1}{4\pi}} \; e^0 \; P_0^0(\cos\theta) = \boxed{\left(\frac{1}{4\pi}\right)^{1/2}}$$

$$Y_2^1 = (-1)^1 \sqrt{\frac{5}{4\pi} \; \frac{1}{3!}} \; e^{i\phi} \; P_2^1(\cos\theta)$$

$$P_2^1(x) = \sqrt{1-x^2} \; \frac{d}{dx} \underbrace{\frac{1}{4 \cdot 2!} \; \frac{d^2}{dx^2} \; (x^2-1)^2}$$

$$\frac{1}{8} \frac{d}{dx}\left[2(x^2-1)(2x)\right] = \frac{1}{4}\left[(2x)^2 + 2(x^2-1)\right] = \frac{3x^2-1}{2}$$

$$P_2^1(x) = \sqrt{1-x^2} \;\; 3x$$

$$Y_2^1 = -\sqrt{\frac{5}{24\pi}} \; e^{i\phi} \; 3\cos\theta \sin\theta = \boxed{-\sqrt{\frac{15}{8\pi}} \; \sin\theta \cos\theta \; e^{i\phi}}$$

$\boxed{\text{HW. [illegible]}}$ AND $\boxed{4.2}$