4. Q.M. in 3D

4.1. Schrödinger Eq.

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi \qquad (1)$$

If V is independent of time $V = V(\vec{r})$

$$\Psi_n(\vec{r}, t) = \varphi_n(\vec{r}) e^{-iE_n t/\hbar}$$

where $$-\frac{\hbar^2}{2m}\nabla^2 \varphi + V\varphi = E\varphi \qquad (2)$$

General solution of (1)

$$\Psi(\vec{r}, t) = \sum_n C_n \varphi_n(\vec{r}) e^{-iE_n t/\hbar} \qquad (3)$$

4.2. spherically symmetric potential $V = V(r)$

Write (2) in spherical coordinates (r, θ, φ)

Eq (2) is separable

$$\varphi(r, \theta, \phi) = R(r)\, Y(\theta, \phi) \qquad (4)$$

Eq (2) reduces to

$$\begin{cases} \dfrac{1}{R}\dfrac{d}{dr}\left(r^2 \dfrac{dR}{dr}\right) - \dfrac{2mr^2}{\hbar^2}\left[V - E\right] = \ell(\ell+1) & (5a) \\[2ex] \dfrac{1}{Y}\left\{\dfrac{1}{\sin\theta}\dfrac{\partial}{\partial\theta}\left(\sin\theta \dfrac{\partial Y}{\partial\theta}\right) + \dfrac{1}{\sin^2\theta}\dfrac{\partial^2 Y}{\partial\phi^2}\right\} = -\ell(\ell+1) & (5b) \end{cases}$$

The angular solutions are $Y_\ell^m(\theta, \phi) \sim P_\ell^m(\cos\theta) e^{im\phi}$

For each ℓ, $\underbrace{m = -\ell, -\ell+1, \ldots, \ell-1, \ell}_{(2\ell+1) \text{ of them}}$

ℓ is an integer for $P_\ell^m(\cos\theta)$ to be finite within [illegible], θ from 0 to π

4.3. Angular functions

The $Y_\ell^m(\theta,\phi)$ or written as $Y_{\ell m}(\theta,\phi)$ in other books are called <u>spherical harmonics</u>.

They are eigenstates of ∇^2 for <u>fixed R</u>. $\Rightarrow$ Surface harmonics.

See eq. (5b) above.

define $\quad d^3\vec{r} = r^2 dr\, d\Omega = r^2 dr\, \underline{\sin\theta\, d\theta\, d\phi} \qquad d\Omega = \sin\theta\, d\theta\, d\phi$

$\{Y_{\ell m}(\theta,\phi)\}$ form a complete set $\quad \begin{cases} \ell = 0, 1, 2, \cdots \\ m = -\ell, \cdots, +\ell \end{cases}$

$$\boxed{\int Y^*_{\ell m}(\theta,\phi)\, Y_{\ell' m'}(\theta,\phi)\, d\Omega = \delta_{\ell\ell'}\,\delta_{mm'}} \qquad (6)$$

Any funtion $f(\theta,\phi)$ on the spherical surface of a 3D space

$$\boxed{f(\theta,\phi) = \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} c_{\ell m}\, Y_{\ell m}(\theta,\phi)} \qquad (7)$$

4.4. The radial eq.

Define $\quad R(r) = \dfrac{u(r)}{r} \qquad (8)$

The radial eq.

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = E\,u \qquad (9)$$

$$V_{eff}(r) = V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$$

centrifugal potential

4.5. Equation of continuity

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2 \Psi + V\Psi \qquad V \text{ is real} \qquad (10a)$$

Take the complex conjugate

$$-i\hbar \frac{\partial \Psi^*}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2 \Psi^* + V\Psi^* \qquad (10b)$$

$$P = P(x,t) = \Psi^* \Psi \qquad (10c)$$

$$\frac{\partial P}{\partial t} = \frac{\partial \Psi^*}{\partial t}\Psi + \Psi^* \frac{\partial \Psi}{\partial t}$$

plug in (10a) and (10b)

$$\frac{\partial P}{\partial t} = \frac{1}{i\hbar}\left[\frac{\hbar^2}{2m}\nabla^2\Psi^* \Psi - \frac{\hbar^2}{2m}\Psi^* \nabla^2 \Psi\right] \qquad (10d)$$

operator identity

$$\nabla\cdot(\varphi \vec{a}) = \vec{a}\cdot\nabla\varphi + \varphi\,\nabla\cdot\vec{a}$$

$$\nabla\cdot(\varphi\nabla\varphi^*) = \nabla\varphi^*\cdot\nabla\varphi + \varphi\nabla^2\varphi$$

$$\nabla\cdot(\varphi^*\nabla\varphi) = \nabla\varphi\cdot\nabla\varphi^* + \varphi^*\nabla^2\varphi$$

$$\frac{\partial P}{\partial t} + \frac{\hbar}{2im}\nabla(\varphi^*\nabla\varphi - \nabla\varphi^*\varphi) = 0 \qquad \varphi = \Psi$$

Messed up.

define $\boxed{\vec{j} = \frac{\hbar}{2im}(\Psi^*\nabla\Psi - \nabla\Psi^*\Psi)}$ ← probability current

$P = \Psi^*\Psi$ density

$$\boxed{\nabla\cdot\vec{j} + \frac{\partial P}{\partial t} = 0} \leftarrow \text{Eq. of Continuity}$$

special mention:

I will not cover spherical harmonics and spherical Bessel functions in the lectures, but you should have some mental pictures how they look alike

(1) For spherical harmonics or associated Legendre functions,

see P. 138.

Essential: $P_\ell^{|m|}(\theta)$, $m=0$ peaks along the z-axis

$|m|=\ell$ peaks perpendicular to the z-axis

Go to web and search images of spherical harmonics, You can find many of them

(2) $\begin{cases} \text{spherical Bessel functions} & j_\ell(x) \\ \text{spherical Neumann functions} & n_\ell(x) \end{cases}$ ℓ integers

see P. 143 for some examples

Important properties:

$x \to 0$ $\begin{cases} j_0(x) \xrightarrow[x\to 0]{} 1 & j_\ell(x) \xrightarrow[x\to 0]{} 0 \quad (\text{for } \ell \neq 0) \\ n_\ell(x) \text{ diverges as } x \to 0 \text{ for all } \ell \end{cases}$

$x \to \infty$ $j_\ell(x) \xrightarrow[x\to\infty]{} \frac{1}{x}\cos\left(x - \frac{\ell+1}{2}\pi\right)$

$n_\ell(x) \to \frac{1}{x}\sin\left(x - \frac{\ell+1}{2}\pi\right)$

To first order, j_ℓ and n_ℓ are similar to cosine and sine functions