LECTURE #8

SCH. EQ. IN 3-D: $i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$

WHERE $H = \frac{p^2}{2m} + V = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V$

$p_x \to \frac{\hbar}{i}\frac{\partial}{\partial x}$, $p_y = \frac{\hbar}{i}\frac{\partial}{\partial y}$, $p_z = \frac{\hbar}{i}\frac{\partial}{\partial z}$ $\Rightarrow$ $\vec{p} \to \frac{\hbar}{i}\nabla$

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

∇^2 IS THE LAPLACIAN. IN CARTESIAN COORDINATES, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$.

NOTE: INCREASING DEGREES OF FREEDOM $\Rightarrow$ INCREASING KINETIC ENERGY

V AND Ψ ARE NOW FUNCTIONS OF $\vec{r} = (x, y, z)$ AND t.

PROBABILITY OF FINDING THE PARTICLE IN THE INFINITESIMAL VOLUME $d\vec{r} = dx\,dy\,dz$ IS $|\Psi(\vec{r},t)|^2 d\vec{r}$

$\Rightarrow$ NORMALIZATION CONDITION IS : $\int |\Psi|^2 d\vec{r} = 1$

INTEGRATE OVER ALL SPACE

IF V IS INDEPENDENT OF TIME (i.e., $V(\vec{r})$),

$$\Psi_n(\vec{r},t) = \psi_n(\vec{r})\, e^{-iE_n t/\hbar}$$ ← STATIONARY STATE

WHERE $\psi_n(\vec{r})$ SATISFIES THE 3-D TIME INDEPENDENT SCH. EQ:

$$-\frac{\hbar^2}{2m}\nabla^2\psi_n + V\psi_n = E_n\psi_n$$

THE GENERAL SOLUTION IS: $\Psi(\vec{r},t) = \sum c_n \psi_n(\vec{r}) e^{-iE_n t/\hbar}$

WHERE C_n IS DETERMINED BY THE INITIAL CONDITIONS $\Psi(\vec{r},0)$

THE 3-D SCH. EQ. IS TYPICALLY SOLVED USING SEPARATION OF VARIABLES IN THE COORDINATE SYSTEM WHERE THE POTENTIAL HAS THE HIGHEST DEGREE OF SYMMETRY.

EXAMPLE: "PARTICLE IN A BOX"

$$\text{i.e., } V(x,y,z) = \begin{cases} 0, & 0 < x,y,z < a \\ \infty, & \text{OTHERWISE} \end{cases}$$

INSIDE THE BOX, THE SCH. EQ. IS: $-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$

TRY SEPARATION OF VARIABLES IN CARTESIAN COORDINATES:

$$\psi(\vec{r}) = X(x)Y(y)Z(z)$$

$$\therefore -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)XYZ = EXYZ$$

$$-\frac{\hbar^2}{2m}YZ\frac{\partial^2 X}{\partial x^2} - \frac{\hbar^2}{2m}XZ\frac{\partial^2 Y}{\partial y^2} - \frac{\hbar^2}{2m}XY\frac{\partial^2 Z}{\partial z^2} = EXYZ$$

$$\underbrace{-\frac{\hbar^2}{2m}\frac{1}{X}\frac{\partial^2 X}{\partial x^2}}_{E_x} \underbrace{-\frac{\hbar^2}{2m}\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}}_{E_y} \underbrace{-\frac{\hbar^2}{2m}\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}}_{E_z} = E$$

NOTE: $E = E_x + E_y + E_z$

$\therefore -\frac{\hbar^2}{2m}\frac{\partial^2 X}{\partial x^2} = E_x X \rightarrow$ THIS IS JUST THE 1-D INFINITE SQUARE WELL

$$\therefore X_{n_x}(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n_x \pi x}{a}\right), \quad E_x = E_{n_x} = \frac{n_x^2 \pi^2 \hbar^2}{2ma^2}$$

Y AND Z ARE ANALOGOUS.

$$\therefore \psi_{n_x n_y n_z}(\vec{r}) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \sin\left(\frac{n_z \pi z}{a}\right)$$

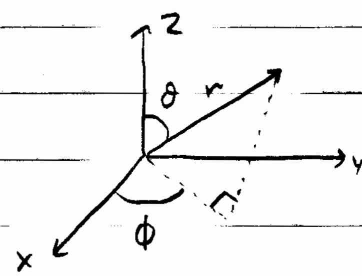
$$E_{n_x n_y n_z} = (n_x^2 + n_y^2 + n_z^2) E_1 \quad \text{WHERE} \quad E_1 = \frac{\pi^2 \hbar^2}{2ma^2}$$

GROUND STATE: $E_{111} = 3E_1$

FIRST EXCITED STATES: $\underbrace{E_{211} = E_{121} = E_{112}}_{\text{NOTE THE 3-FOLD DEGENERACY}} = (2^2 + 1^2 + 1^2)E_1 = 6E_1$

SPHERICALLY SYMMETRIC POTENTIALS: $V(r)$, $r = |\vec{r}|$

SPHERICAL COORDINATES:



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

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

$z = r\cos\theta$

$x^2 + y^2 + z^2 = r^2$, $d\vec{r} = r^2 \sin\theta \, dr \, d\theta \, d\phi$

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

SEPARATION OF VARIABLES: $\psi(\vec{r}) = R(r)\, Y(\theta,\phi)$

$$\therefore \frac{-\hbar^2}{2m}\left[Y \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R + R\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)Y\right.$$
$$\left. + R\frac{1}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] + VRY = ERY$$

DIVIDE BY RY AND MULTIPLY BY $\frac{-2mr^2}{\hbar^2}$

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

RADIAL EQUATION:

$$\therefore \frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}\left[V(r)-E\right] = \text{CONSTANT} = \ell(\ell+1)$$

ANGULAR EQUATION:

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

NOTE: THE ANGULAR EQUATION IS NOT A FUNCTION OF V, THUS WE ONLY HAVE TO SOLVE IT ONCE.

MULTIPLY BY $Y\sin^2\theta$:

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

SEPARATION OF VARIABLES: $Y(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$

$$\therefore \underbrace{\frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right]+\ell(\ell+1)\sin^2\theta}_{\text{ONLY A FUNCTION OF } \theta} = \underbrace{-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}}_{\text{ONLY A FUNCTION OF } \phi}$$

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

$$-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = m^2 \Rightarrow \Phi = e^{im\phi}$$

NOTE: ϕ AND $\phi+2\pi$ ARE THE SAME POINT IN SPACE

$$\therefore\ \Phi(\phi+2\pi) = \Phi(\phi) \Rightarrow e^{i2\pi m} = 1 \Rightarrow m = 0, \pm 1, \pm 2, \ldots$$

↳ "MAGNETIC QUANTUM NUMBER"

SOLVE THE Θ EQUATION:

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

THE SOLUTION IS: $\Theta(\theta) = A\, P_\ell^m(\cos\theta)$

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

← ASSOCIATED LEGENDRE FUNCTION

AND $P_\ell(x) = \frac{1}{2^\ell \ell!}\left(\frac{d}{dx}\right)^\ell (x^2-1)^\ell$ — "RODRIGUES FORMULA"

↳ ℓ^{th} LEGENDRE POLYNOMIAL

"AZIMUTHAL QUANTUM NUMBER"

SEE TABLES 4.1 AND 4.2   NOTE: $\boxed{\ell = 0, 1, 2, \ldots}$

SINCE $P_\ell(x)$ IS A POLYNOMIAL OF DEGREE ℓ, WE SEE THAT $P_\ell^m(x)$ IS NONZERO ONLY IF: $\boxed{|m| \le \ell}$

i.e., $m = -\ell, -\ell+1, \ldots, 0, \ldots, \ell-1, \ell$

$\Rightarrow 2\ell+1$ DIFFERENT m's

$$\therefore\ Y_\ell^m(\theta,\phi) = A\, P_\ell^m(\cos\theta)\, e^{im\phi}, \quad A: \text{NORMALIZATION CONSTANT}$$

← SPHERICAL HARMONICS

THEY ARE NORMALIZED SUCH THAT: $\int_0^{2\pi}\int_0^{\pi} |Y_\ell^m|^2 \sin\theta\, d\theta\, d\phi = 1$

THEY ARE ALSO ORTHOGONAL:

$$\int_0^{2\pi}\int_0^{\pi} Y_\ell^{m*}\, Y_{\ell'}^{m'} \sin\theta\, d\theta\, d\phi = \delta_{\ell\ell'}\,\delta_{mm'} = \begin{cases} 1 & \text{IF } \ell=\ell' \text{ \underline{AND} } m=m' \\ 0 & \text{OTHERWISE} \end{cases}$$

$\boxed{\text{SEE TABLE 4.3}}$

<u>RADIAL EQUATION</u>:

PARTICLE MASS - NOT MAGNETIC QUANTUM #

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

LET $u(r) = r R(r)$ $\quad$ $u =$ "RADIAL WAVEFUNCTION"

$$\Rightarrow \quad R = \frac{u}{r}, \quad \frac{dR}{dr} = -\frac{u}{r^2} + \frac{1}{r}\frac{du}{dr}$$

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = \frac{d}{dr}\left(-u + r\frac{du}{dr}\right) = -\frac{du}{dr} + \frac{du}{dr} + r\frac{d^2u}{dr^2} = r\frac{d^2u}{dr^2}$$

$\therefore$ RADIAL EQUATION BECOMES:

$$r\frac{d^2u}{dr^2} - \frac{2mr}{\hbar^2}(V-E)u = \ell(\ell+1)\frac{u}{r}$$

MULTIPLY BY $\frac{-\hbar^2}{2mr}$:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \Big[V + \underbrace{\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}}_{\text{"CENTRIFUGAL TERM"}}\Big]u = Eu$$

LOOKS LIKE THE 1-D SCH. EQ PLUS AN ADDITIONAL CENTRIFUGAL TERM THAT TENDS TO THROW THE PARTICLE AWAY FROM THE ORIGIN.

IN SUMMARY, FOR <u>ANY</u> SPHERICALLY SYMMETRIC POTENTIAL,

STATIONARY STATES: $\Psi(\vec{r},t) = \psi(\vec{r})\, e^{-iEt/\hbar}$

WHERE $\psi(\vec{r}) = R(r)\, \underbrace{Y_\ell^m(\theta,\phi)}_{\text{"SPHERICAL HARMONICS"}}$, $\ell = 0,1,2,\ldots;\ |m| \le \ell$

AND $u = rR$ SATISFIES THE RADIAL EQUATION

<u>NORMALIZATION</u>: $\int |\psi(\vec{r})|^2 d\vec{r} = 1$

$$\Rightarrow \int_0^\infty \underbrace{|R|^2 r^2 dr}_{|u|^2} \underbrace{\int_0^{2\pi}\int_0^\pi |Y_\ell^m|^2 \sin\theta\, d\theta\, d\phi}_{=1}$$

$$\therefore \int_0^\infty |u|^2 dr = 1$$

<u>EXAMPLE</u>: INFINITE SPHERICAL WELL:

i.e., $V(r) = \begin{cases} 0, & r \le a \\ \infty, & r > a \end{cases}$

RADIAL EQUATION INSIDE THE WELL:

$$\frac{d^2u}{dr^2} = \left[\frac{\ell(\ell+1)}{r^2} - k^2\right]u \quad \text{WHERE } k = \frac{\sqrt{2mE}}{\hbar}$$

<u>CONSIDER $\ell = 0$</u>: $\frac{d^2u}{dr^2} = -k^2 u \Rightarrow u(r) = A\sin(kr) + B\cos(kr)$

BUT, $R = \frac{u}{r} \Rightarrow \frac{\cos(kr)}{r}$ BLOWS UP AS $r \to 0 \Rightarrow B = 0$

BOUNDARY CONDITION: $u(a)=0 \Rightarrow \sin(ka)=0 \Rightarrow ka=\pi, 2\pi, \ldots$

$$\therefore \boxed{E_{n0} = \frac{n^2\pi^2\hbar^2}{2ma^2}, \quad n=1,2,\ldots}$$

SAME AS 1-D INFINITE SQUARE WELL

NORMALIZE: $\int |u|^2 dr = 1$

AGAIN IT IS THE SAME AS 1-D INFINITE SQUARE WELL

$$\Rightarrow A = \sqrt{\frac{2}{a}}$$

SPHERICAL HARMONIC: $\ell=0 \Rightarrow m=0 \Rightarrow Y_0^0(\theta,\phi) = \frac{1}{\sqrt{4\pi}}$

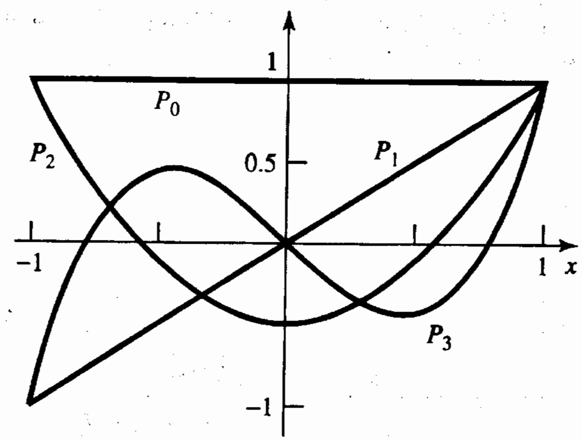
$$\therefore \boxed{\psi_{n00} = \frac{1}{\sqrt{2\pi a}} \frac{\sin(n\pi r/a)}{r}}$$

FOR $\ell \neq 0$, THE SOLUTIONS ARE BESSEL FUNCTIONS (SEE GRIFFITHS, SEC. 4.1)

TABLE 4.1: The first few Legendre polynomials, $P_l(x)$: (a) functional form, (b) graphs.

$$P_0 = 1$$
$$P_1 = x$$
$$P_2 = \frac{1}{2}(3x^2 - 1)$$
$$P_3 = \frac{1}{2}(5x^3 - 3x)$$
$$P_4 = \frac{1}{8}(35x^4 - 30x^2 + 3)$$
$$P_5 = \frac{1}{8}(63x^5 - 70x^3 + 15x)$$

(a)

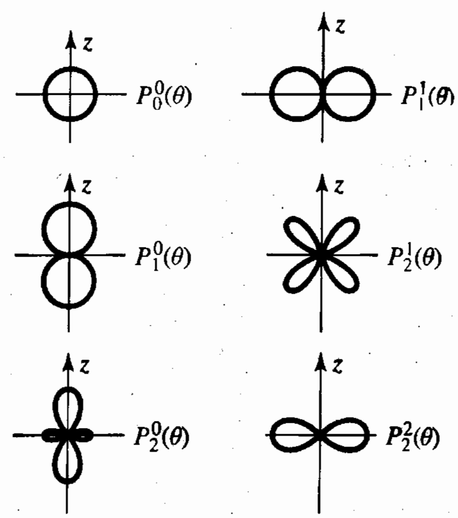


(b)

TABLE 4.2: Some associated Legendre functions, $P_l^m(\cos\theta)$: (a) functional form, (b) graphs of $r = P_l^m(\cos\theta)$ (in these plots r tells you the magnitude of the function in the direction θ; each figure should be rotated about the z-axis).

$P_0^0 = 1$	$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$
$P_1^1 = \sin\theta$	$P_3^3 = 15\sin\theta(1 - \cos^2\theta)$
$P_1^0 = \cos\theta$	$P_3^2 = 15\sin^2\theta\,\cos\theta$
$P_2^2 = 3\sin^2\theta$	$P_3^1 = \frac{3}{2}\sin\theta(5\cos^2\theta - 1)$
$P_2^1 = 3\sin\theta\,\cos\theta$	$P_3^0 = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)$

(a)



(b)

TABLE 4.3: The first few spherical harmonics, $Y_l^m(\theta, \phi)$.

$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$	$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$
$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$	$Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$
$Y_1^{\pm 1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$	$Y_3^{\pm 1} = \mp\left(\frac{21}{64\pi}\right)^{1/2} \sin\theta\,(5\cos^2\theta - 1)e^{\pm i\phi}$
$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$	$Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta\cos\theta e^{\pm 2i\phi}$
$Y_2^{\pm 1} = \mp\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{\pm i\phi}$	$Y_3^{\pm 3} = \mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}$

The normalized angular wave functions[8] are called **spherical harmonics**:

$$\boxed{Y_l^m(\theta, \phi) = \epsilon\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}\, e^{im\phi}\, P_l^m(\cos\theta),} \qquad [4.32]$$