project:
4-1

$\boxed{\text{Ch 4 QM in 3d}}$

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\Psi(x)=i\hbar\frac{\partial\Psi}{\partial t}$$

$$x \to \vec{r}=(x\,y\,z)$$

$$\frac{\partial^2}{\partial x^2} \to \nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

As in $d=1$ $\quad \Psi(xt) \to \psi_n(x)e^{-iE_nt/\hbar}$

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi_n(x)=E_n\psi_n(x)$$

$$\Psi(xt)=\sum c_n\psi_n(x)e^{-iE_nt/\hbar}$$

$$c_n=\int\psi_n^*(x)\Psi(x,0)\,dx$$

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

$$c_n=\int\psi_n^*(\vec{r})\Psi(\vec{r},0)\,d^3r$$

Stay in x,y,z if $V(\vec{r})$ has rectangular symmetry eg 3d well

$$V(\vec{r})=\begin{cases}0 & 0<x<a \quad 0<y<b \quad 0<z<c\\ \infty & \text{otherwise}\end{cases}$$

$$\psi_n(x,y,z)=\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}\sqrt{\frac{2}{b}}\sin\frac{m\pi y}{b}\sqrt{\frac{2}{c}}\sin\frac{\ell\pi z}{c}$$

Problem 4-2
$a=b=c$

DIVOGA $\quad E_n=\frac{\hbar^2\pi^2}{2ma^2}(n^2+m^2+\ell^2)$

project:
4-2

But more often $V(\vec{r}) = V(r)$ $\quad r = (x^2+y^2+z^2)^{1/2}$

Most prominently the H atom.

Same as Kepler problem

Then want to use r, θ, ϕ

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

$$+ V\psi = E\psi$$

<u>Guess</u>: $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$ put in Sch Eqn + divide by RY

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

$$+ \frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\} = 0$$

r only

θ, ϕ only

so $\{\ \}_1 = l(l+1)$

$\{\ \}_2 = -l(l+1)$

Separation constant written so looks simple later

Look at angular Eqn (multiply by $\sin^2\theta\, Y$)

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

Again separate variables $\quad Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$

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

$\Phi(\phi) = e^{im\phi}$ $\qquad$ m integer required by $\Phi(\phi+2\pi) = \Phi(\phi)$

Messy Eqn for $\Theta(\theta)$

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

Not too much to say here, it's just a bit yechy!

Answer is $\quad \Theta(\theta) = P_\ell^m(\cos\theta)$

$\uparrow$ associated Legendre function

$$P_\ell(x) = \frac{1}{2^\ell \ell!}\left(\frac{d}{dx}\right)^\ell (x^2-1)^\ell \quad \leftarrow \text{Legendre polynomial}$$

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

4-4

P_0 $\quad 1$

P_1 $\quad x$ $\qquad$ Polys

P_2 $\quad \frac{1}{2}(3x^2-1)$

P_3 $\quad \frac{1}{2}(5x^3-3x)$

$$P_2^0(x) = P_2(x) = \frac{1}{2}(3x^2-1)$$

$$P_2^1(x) = (1-x^2)^{1/2} \frac{d}{dx}\left[\frac{1}{2}(3x^2-1)\right] = 3x\sqrt{1-x^2}$$

$$P_2^1(\cos\theta) = 3\sin\theta\cos\theta$$

Check it out!!

$$\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{dP_\ell^m(\cos\theta)}{d\theta}\right) + \left[\ell(\ell+1)\sin^2\theta - m^2\right]P_\ell^m(\cos\theta) \overset{?}{=} 0$$

$\left.\begin{matrix} \ell=2 \\ m=1 \end{matrix}\right\}$

$$\sin\theta \frac{d}{d\theta}\left(\sin\theta\, \cancel{3}(\underbrace{\cos^2\theta - \sin^2\theta}_{1-2\sin^2\theta})\right) + (6\sin^2\theta - 1)\cancel{3}\sin\theta\cos\theta \overset{?}{=} 0$$

$$\sin\theta\left(\cos\theta - 6\sin^2\theta\cos\theta\right) + (6\sin^2\theta - 1)\sin\theta\cos\theta \overset{?}{=} 0$$

$$\sin\theta\cos\theta(1 - 6\sin^2\theta) + (6\sin^2\theta - 1)\sin\theta\cos\theta \overset{?}{=} 0 \checkmark$$

So it works ...

4-5 See Griffiths page 139

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$Y_1^{\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin\theta \, e^{\pm i\phi}$$

Normalization

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta \, |Y_\ell^m|^2 = 1$$

$$\int_0^{\infty} |R^2| \, r^2 dr = 1$$

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

$$\epsilon = (-1)^m \quad m \geq 0$$

$$= 1 \quad m \leq 0$$

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

Mathematical Sidelight

For what sorts of 2nd order differential operators are the eigenfunctions orthogonal?

Our experience answers: for operators which are **Hermitian**,

"Sturm Liouville Theory" provides unifying element for many of the "special functions" of mathematical physics

Consider $$\mathcal{L}\, u(x) = \underbrace{\left[p_0(x) \frac{d^2}{dx^2} + p_1(x) \frac{d}{dx} + p_2(x) \right]}_{\text{2nd order linear differential operator } \mathcal{L}} u(x)$$

p_0, p_1, p_2 polynomials

$$\langle u | \mathcal{L} | v \rangle = \int dx\, u(x) \left[p_0 \frac{d^2 v}{dx^2} + p_1 \frac{dv}{dx} + p_2 v \right]$$

Integrate by parts and insist bdy terms vanish eq

$$= \int dx \left(-\frac{d}{dx}(p_0 u) \frac{dv}{dx} - \frac{d}{dx}(p_1 u)\, v + p_2 v \right)$$

$$= \int dx\, v(x) \left[\frac{d^2}{dx^2} p_0 u - \frac{d}{dx} p_1 u + p_2 u \right]$$

$$= \int dx\, v(x) \left[p_0 \frac{d^2 u}{dx^2} + p_1 \frac{du}{dx} + p_2 u \right.$$

$$\left. + \underbrace{\frac{d^2 p_0}{dx^2} u + 2 \frac{dp_0}{dx} \frac{du}{dx} - 2 p_1 \frac{du}{dx} - \frac{dp_1}{dx} u}_{\text{will vanish if } p_1 = dp_0/dx} \right]$$

$$= \langle v | \mathcal{L} | u \rangle$$

"Hermitian"

Thus any $\mathcal{L} = p_0(x)\frac{d^2}{dx^2} + p_1(x)\frac{d}{dx} + p_2(x)$

with $p_1 = dp_0/dx$ is Hermitian

Legendre
Bessel
Laguerre
Hermite
Chebyshev

$\Big\}$ All examples with different $p_0\ p_1\ p_2$!

Eg Legendre $p_0(x) = 1-x^2$
$p_1(x) = -2x$
$p_2(x) = \ell(\ell+1)$

Actually a bit more complicated "weight function"

Simplest (most familiar example
are Fourier series !

$\mathcal{L} = \frac{d^2}{dx^2} + k^2$ $\quad$ $p_0(x) = 1$, $p_1(x) = 0$, $p_2(x) = +k^2$ $\Big\}$ $p_1 = \frac{dp_0}{dx}$ ✓✓

guarantees $\sin kx$ $\cos kx$ are $\perp$!

eg $\frac{2}{L}\int_0^L \sin\frac{n\pi x}{L} \sin\frac{m\pi x}{L}\, dx = \delta_{nm}$