

Q.M. story ...

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

is always eigenstates

$$\hat{H}\Psi = E\Psi$$

$$\Psi = e^{-i \frac{E}{\hbar} t} \psi(x) = \text{stationary states}$$

ψ = good complete basis
for even time dep part

$[\hat{H}, \hat{A}] = 0$ means observables of \hat{A}, a , also eigenvalue of energy eigenstates

all

1-D so far ...

recall $\Psi(x,t)$ Born prob condition

$$\int_{-\infty}^{+\infty} \Psi^*(x,t) \Psi(x,t) dx = 1$$

must consider Ψ over all of 1-D space

now in 3-D $\Psi(x,y,z,t)$

$$\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \Psi^*(x,y,z,t) \Psi(x,y,z,t) dx dy dz = 1$$

$$= \int_{-\infty}^{+\infty} \Psi^* \Psi d^3\vec{r} = 1$$

The entire formalism, including expectations follows ...

$$\langle \hat{A} \rangle = \int_{-\infty}^{+\infty} \Psi^* \hat{A} \Psi d^3\vec{r}$$

and \Rightarrow

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

$$\hat{H}\Psi(x,y,z) = E\Psi(x,y,z)$$

$$\psi(x,y,z,t) = e^{-i\frac{Et}{\hbar}} \psi(x,y,z)$$

So that's the plan

$\hat{H}\Psi(x,y,z) = E\Psi(x,y,z)$ is Cartesian
Symmetry
or whatever coordinates
are most convenient

$\hat{H}\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi) =$ Spherical
Symmetry

$\hat{H}\Psi(r,\phi,z) = E\Psi(r,\phi,z) =$ Cylindrical
Symmetry

Of course, $\hat{H} = E_T = \frac{p^2}{2m} + V + \text{anything else}$

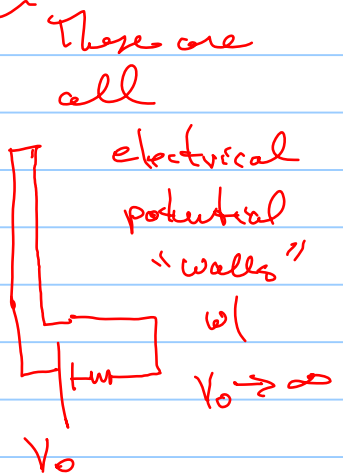
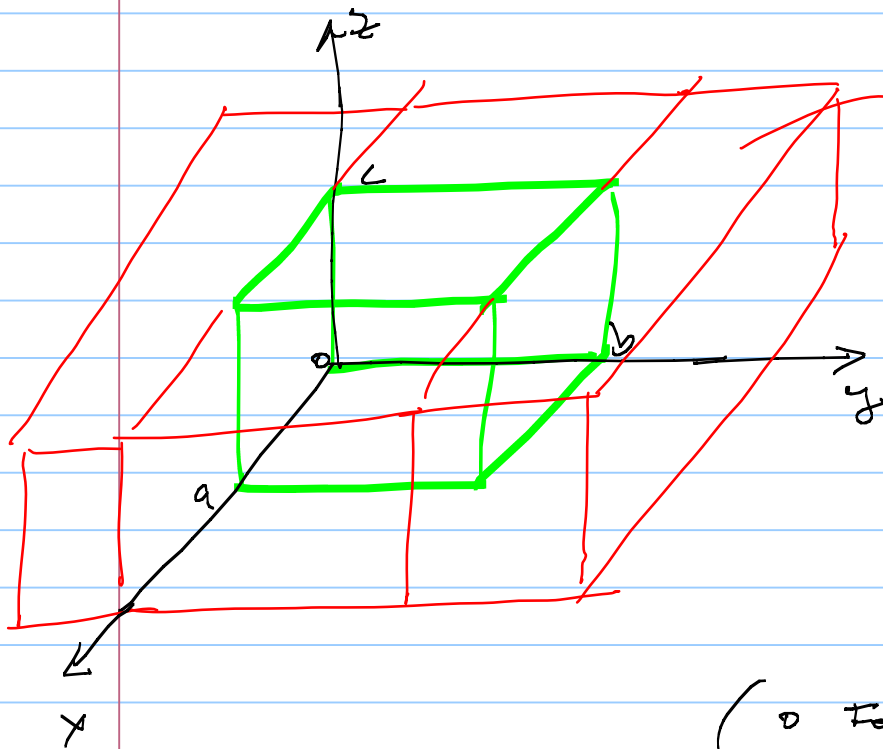
most

also be expressed
in these coordinates

3D

3-D Schrödinger - Indep Problem =

Particle
in
 ∞ -
3-D
Box!



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

and

Clearly... the cartesian symmetry is most convenient coordinate system to use.

OK you've got 3-D $V(\vec{r})$

Recall for 3-D $\frac{\hat{p}^2}{2m}$

$$* \quad -\hbar^2 \frac{\partial^2}{\partial x^2} = 1-D \quad \frac{\hat{p}^2}{2m}$$

$$- \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} = 1-D \quad \frac{\hat{p}^2}{2m}$$

$$\text{So } 3\text{-D } \vec{p} = -i\hbar \left(\frac{\partial}{\partial x} \hat{i} + \frac{\partial}{\partial y} \hat{j} + \frac{\partial}{\partial z} \hat{k} \right)$$

or $-i\hbar \vec{\nabla}$ "Del" operator

$$\text{now } E_n = \frac{p^2}{2m} \text{ so } 3\text{-D } = \frac{\vec{p} \cdot \vec{p}}{2m}$$

$$\frac{(-i\hbar)^2 \vec{\nabla} \cdot \vec{\nabla}}{2m} =$$

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

$$= -\frac{\hbar^2}{2m} \nabla^2$$

$$\text{OK: } \hat{H} \psi_n(x,y,z) = E_n \psi_n(x,y,z)$$

already anticipating
Quantized energy
energies!

$$= \left(-\frac{\hbar^2}{2m} \nabla^2 + V(x,y,z) \right) \psi_n(x,y,z) = E_n \psi_n$$

$$= \frac{-\hbar^2}{2m} \left(\frac{\partial^2 \psi_n}{\partial x^2} + \frac{\partial^2 \psi_n}{\partial y^2} + \frac{\partial^2 \psi_n}{\partial z^2} \right) + V \psi_n = E_n \psi_n$$

OK
↓

$$\frac{\partial^2 \psi_n}{\partial x^2} + \frac{\partial^2 \psi_n}{\partial y^2} + \frac{\partial^2 \psi_n}{\partial z^2} = -\frac{2mE_n}{\hbar^2} \psi_n \leftarrow$$

OK... what next? solve for $\psi_n(x, y, z)$
How?

Separation of variables \Rightarrow good place
to start & build a general bases set

OK $\psi_n(x, y, z) = \psi_x(x) \psi_y(y) \psi_z(z)$

Same old thing sub into orig prob

$$\psi_y(y) \psi_z(z) \frac{\partial^2 \psi_x}{\partial x^2} + \psi_x(x) \psi_z(z) \frac{\partial^2 \psi_y}{\partial y^2} + \psi_x(x) \psi_y(y) \frac{\partial^2 \psi_z}{\partial z^2} = \frac{-2mE_n \psi_n}{\hbar^2}$$

Next again, some old trick

div. de everything by $\psi_x \psi_y \psi_z$

$$\frac{1}{\psi_x} \frac{\partial^2 \psi_x}{\partial x^2} + \frac{1}{\psi_y} \frac{\partial^2 \psi_y}{\partial y^2} + \frac{1}{\psi_z} \frac{\partial^2 \psi_z}{\partial z^2} = \frac{-2mE_n}{\hbar^2}$$

New watch

$$\psi(x) + \psi(y) + \psi(z) = \frac{-2mE_n}{\hbar^2}$$

$$a) \quad \psi(x) = \frac{-2mE_n}{\hbar^2} - \psi(y) - \psi(z)$$

or

$$b) \quad \psi(y) = \frac{-2mE_n}{\hbar^2} - \psi(x) - \psi(z)$$

or

$$c) \quad \psi(z) = \frac{-2mE_n}{\hbar^2} - \psi(x) - \psi(y)$$

Now as before, if x, y & z are independent variables

say

$$\psi(x=z) = \frac{-2mE_n}{\hbar^2} - \psi(y=\text{anything}) - \psi(z=\text{anything})$$

only way that this can happen is

is each, $\psi(x), \psi(y)$ & $\psi(z)$ are = to constants!

OR:

$$\frac{1}{\psi_x} \frac{d^2\psi_x}{dx^2} = C_x$$

$$\frac{1}{\psi_y} \frac{d^2\psi_y}{dy^2} = C_y$$

$$\frac{1}{\psi_z} \frac{d^2\psi_z}{dz^2} = C_z$$

This is only way
a, b & c could
be
TRUE!

So ...

recurrence

$$\frac{1}{\psi_x} \frac{d^2 \psi_x}{dx^2} + \frac{1}{\psi_y} \frac{d^2 \psi_y}{dy^2} + \frac{1}{\psi_z} \frac{d^2 \psi_z}{dz^2} = \frac{-2mE}{\hbar^2}$$

$$C_x + C_y + C_z = \frac{-2mE_n}{\hbar^2}$$

Now

so maybe

$$\frac{-\hbar^2}{2m} [C_x + C_y + C_z] = E_n$$

$$E_x = \frac{-\hbar^2}{2m} C_x$$

$$E_y = \frac{-\hbar^2}{2m} C_y$$

$$E_z = \frac{-\hbar^2}{2m} C_z$$

So ...

$$\frac{1}{\psi_x} \frac{d^2 \psi_x}{dx^2} = C_x = \frac{2m}{\hbar^2} E_x$$

$$\frac{1}{\psi_y} \frac{d^2 \psi_y}{dy^2} = C_y = \frac{2m}{\hbar^2} E_y$$

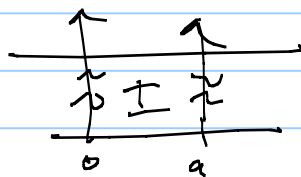
$$\frac{1}{\psi_z} \frac{d^2 \psi_z}{dz^2} = C_z = \frac{2m}{\hbar^2} E_z$$

For x:

$$\psi_x'' = \frac{2m}{\hbar^2} E_x \psi_x$$

$$\psi_x'' + \frac{2m}{\hbar^2} E_x \psi_x \Rightarrow \text{Look Familiar?}$$

of course... 1-D Schrödinger, 1-D ∞ well



$$\hat{H}\psi_n = E_n \psi_n$$

Region I only

$$\psi'' + A\psi = 0$$

$$A = \frac{2m}{\hbar^2} (E_n - V) \rightarrow 0$$

we get $\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \quad 0 \leq x \leq a$
 otherwise 0

$$E_n = \frac{\hbar^2 \pi^2}{2ma^2} n^2; \quad n=1,2,3,\dots$$

So:

$$\psi_x(x) \propto \sin\left(\frac{n_x \pi x}{a}\right) \quad w/ \quad E_{n_x} = \frac{\hbar^2 \pi^2}{2ma^2} n_x^2$$

* note

$n = \#$ of $\frac{1}{2} \lambda$'s now in 3-D!

So 3-D particle has to fit $\frac{1}{2} \lambda$'s in all 3-directions

$$\psi_y(y) \propto \sin\left(\frac{n_y \pi y}{b}\right) \quad w/ \quad E_{n_y} = \frac{\hbar^2 \pi^2}{2mb^2} n_y^2$$

$$\psi_z(z) \propto \sin\left(\frac{n_z \pi z}{c}\right) \quad w/ \quad E_{n_z} = \frac{\hbar^2 \pi^2}{2mc^2} n_z^2$$

Therefore... particle in
3-D potential Box

$$\hat{H} \psi_n = E_n \psi_n$$

$$\psi_{(n_x, n_y, n_z)} = \psi_x(x) \psi_y(y) \psi_z(z)$$

$$= A \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

\uparrow
 toss all the constants together into 1 Big constant
 $= \sqrt{\frac{8}{\text{Volume}}} = \sqrt{\frac{8}{abc}}$
 = H.W. prob 6.1
 that will have to be our normalized constant anyway

$$w) \quad E_{(n_x, n_y, n_z)} = E_x + E_y + E_z = \left(\frac{\hbar^2 \pi^2}{2m}\right) \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

$$\left. \begin{array}{l} n_x = 1, 2, 3, \dots \\ n_y = 1, 2, 3, \dots \\ n_z = 1, 2, 3, \dots \end{array} \right\} \text{all independently!}$$

That's it! Looks like 3 linearly indep 1-D solns multiplied together!
 $\frac{1}{2}$ it is!

* $n_x, n_y, n_z = \neq \frac{1}{2}$ wavelengths that fit in that direction.

* Last pt \downarrow

Check out if Box = cube, $a=b=c$

Then

$$E_n = \frac{\hbar^2 \pi^2}{2ma^2} (n_x^2 + n_y^2 + n_z^2)$$

$$\psi_{(n_x, n_y, n_z)} = \sqrt{\frac{8}{a^3}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \sin\left(\frac{n_z \pi z}{a}\right)$$

note if $n_x=1$
 $n_y=1$
 $n_z=2$ } $\psi_{1,1,2}$ & $E_{1,1,2}$

then $n_x=1$
 $n_y=2$
 $n_z=1$ } $\psi_{1,2,1}$ & $E_{1,2,1}$

Note $\psi_{1,1,2} \neq \psi_{1,2,1}$

But $E_{1,1,2} = E_{1,2,1}$

This happens often! That for 2 different wave functions

$$\psi_a \neq \psi_b = \text{Degenerate}$$

But $E_a = E_b$ energy states:
Same energy, different wavefunctions!

Modes \Rightarrow

Degeneracies appear when there are symmetries!

(Ube = very symmetric)

Symmetric system

$\left. \begin{matrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{matrix} \right\}$ all not equal but $E_1 = E_2 = E_3$

Now if you break the symmetry somehow.

$E_1 \neq E_2 \neq E_3$

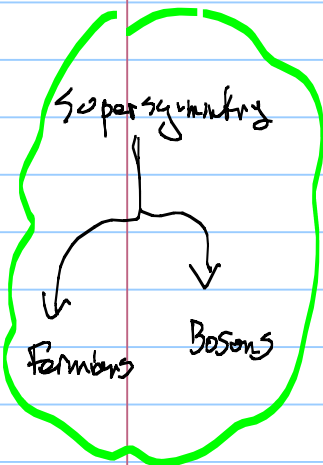
all

look

different!

Wow!

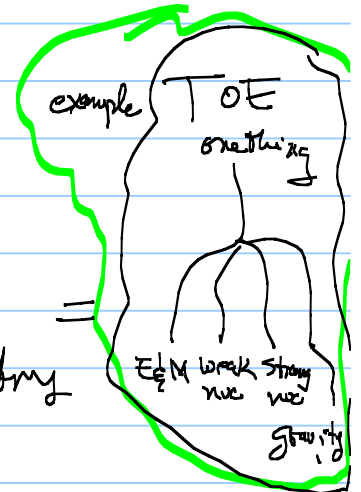
Now BIGGER PICTURE



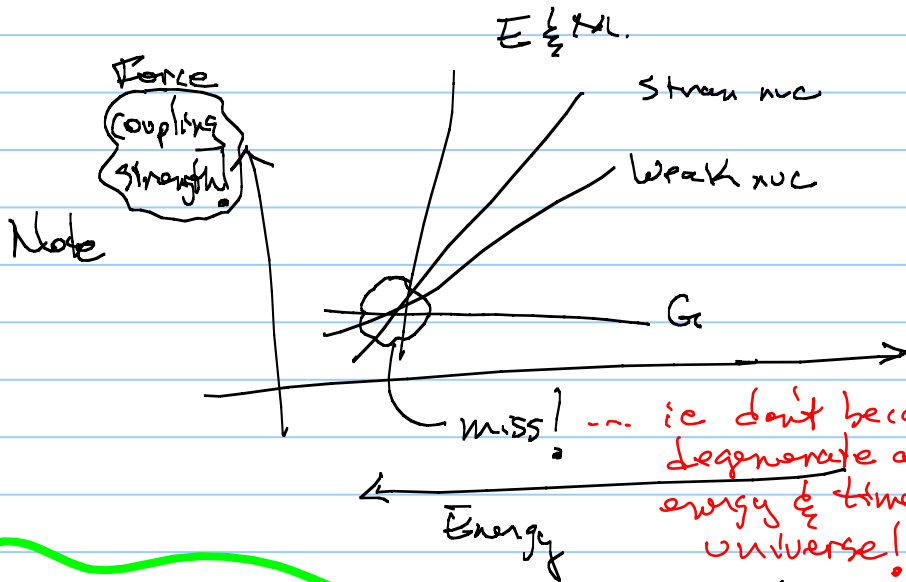
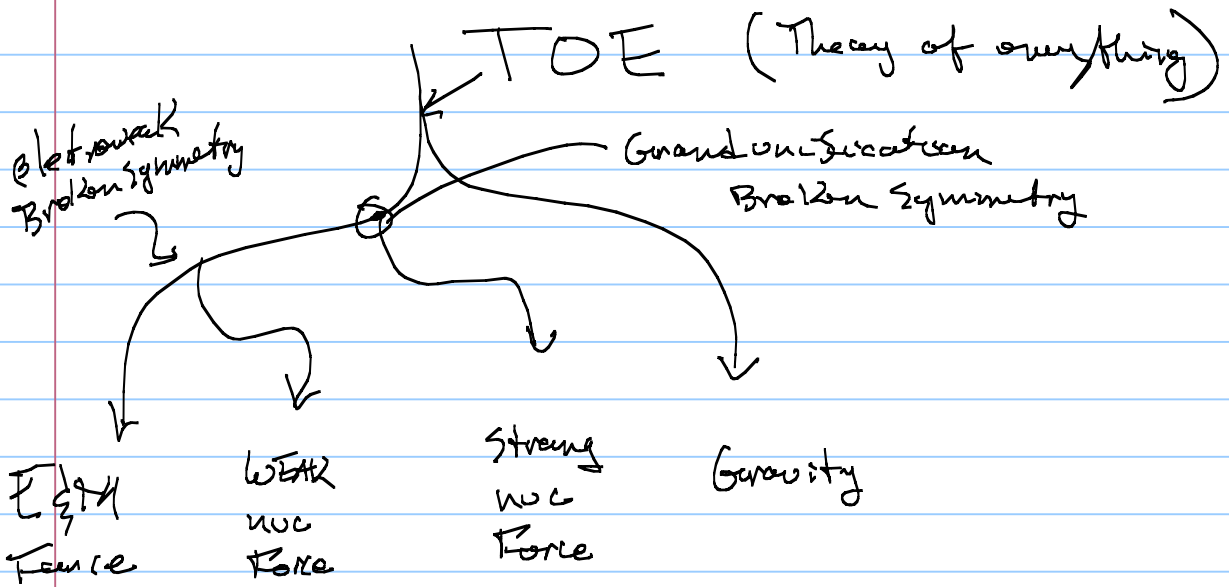
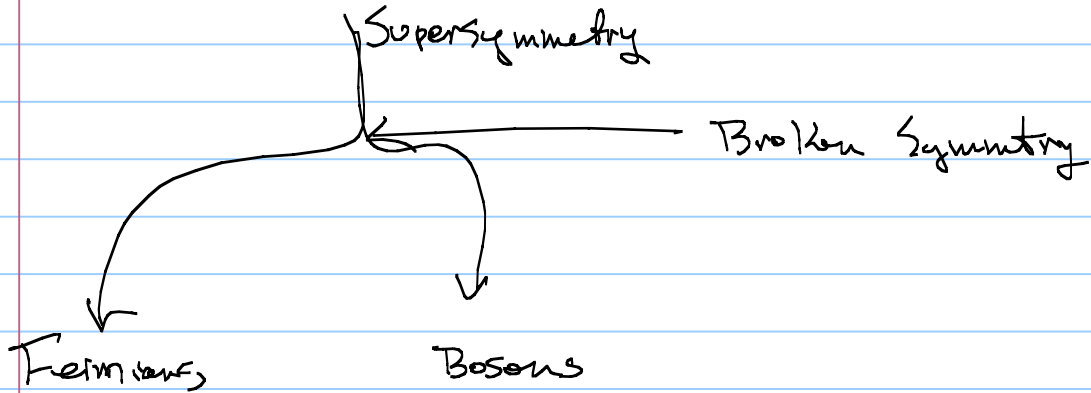
VERY SYMMETRIC
($\psi_1, \psi_2 \dots \psi_n$)
all same E

Break Symmetry

$\left. \begin{matrix} \psi_1 & \psi_2 & \dots & \psi_n \\ E_1 & E_2 & \dots & E_n \end{matrix} \right\}$ Everything look
different



ex:



Job is make super symmetric they meet EXACTLY!

HUGE!