We have now seen 3 different, equivalent ways to represent the wavefunction:

$$\Psi(x,t) \quad , \quad \Phi(p,t) \quad , \quad \{c_n\}$$

$$\Psi(x,t) = \langle x \mid \Psi \rangle \quad g_x$$

$$\Phi(p,t) = \langle p \mid \Psi \rangle \quad f_p$$

$$\{c_n\} = \{ \langle \psi_n \mid \Psi \rangle \}$$

$\{c_n\}$ looks different than functions Ψ and Φ, but not really: $\{c_n\}$ is an infinite set of numbers that associate a number (c_n) with a "coordinate" n. Likewise $\Psi(x,t)$ is ∞ set of nbrs that associate a nbr $\Psi(x)$ with a coordinate x.

Multiple ways to represent the "state" of the system, like multiple ways to represent a ordinary vector:

$$\vec{v} = (v_x, v_y, v_z) = (v_{x'}, v_{y'}, v_{z'}) = (v_r, v_\theta, v_\varphi)$$

There is a vector $\vec{v}$ which exists independent of its representation in any particular basis. Likewise, there is a "state vector" $|S\rangle$ or $|\Psi\rangle$ which exists "out there" in an abstract Hilbert space, independent of any representation

Dirac's Notation: abstract state vector $= |\Psi\rangle$ (or $|S\rangle$ to avoid confusion w/ $\Psi(x)$)

$|\Psi\rangle$ is called a "ket" because it is the right hand side of a "brac·ket" $\langle \psi_n | \Psi \rangle$

Before continuing w/ formal math structure of QM, let's pause and make the leap from 1D to 3D

1D $\longrightarrow$ 3D:

$$x \rightarrow \vec{r} = (x, y, z) \quad , \quad \Psi(x) \longrightarrow \Psi(\vec{r})$$

$$\int_{\text{all } x} |\Psi(x)|\, dx = 1 \longrightarrow \int_{\substack{\text{all}\\ \text{space}}} |\Psi(\vec{r})|^2\, d^3\vec{r}$$

↖ volume element

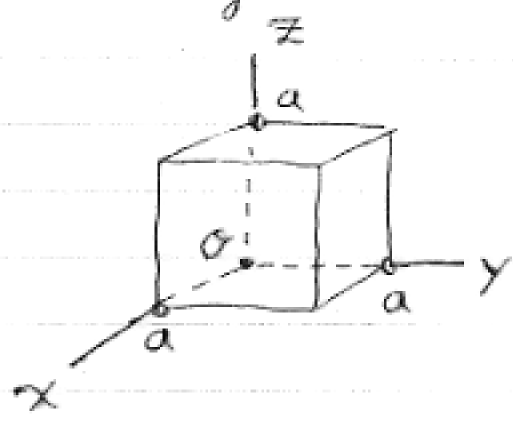
$$\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x} \longrightarrow \hat{\vec{p}} = \frac{\hbar}{i}\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$$

$$V(x) \longrightarrow V(\vec{r})$$

$$\hat{H}_x = \frac{\hat{p}_x^2}{2m} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \longrightarrow \hat{H} = \frac{\hat{\vec{p}} \cdot \hat{\vec{p}}}{2m} = \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

Simplest example: Particle in a 3D box (surprising good approx. for describing conduction electron in a metal.)

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



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

Separation of Variables: $\Psi(\vec{r}, t) = \psi(\vec{r})\,\varphi(t)$

$$\Rightarrow \hat{H}\psi(\vec{r}) = E\,\psi(\vec{r}) \quad , \quad \varphi(t) = e^{-iEt/\hbar}$$

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

Sep. of Var. (again!). Search for sol'ns of form

$$\psi(x,y,z) = \psi_1(x)\cdot\psi_2(y)\cdot\psi_3(z)$$

Plug into TISE and divide thru by $\psi_1\psi_2\psi_3$.

$$\left[\frac{1}{\psi_1\psi_2\psi_3}\frac{\partial^2}{\partial x^2}[\psi_1(x)\psi_2\psi_3] = \frac{1}{\psi_1}\frac{d^2\psi_1(x)}{dx^2} = \frac{\psi_1''(x)}{\psi_1}, \text{etc}\right]$$

$\Rightarrow$

$$-\frac{\hbar^2}{2m}\left(\underbrace{\frac{\psi_1''(x)}{\psi_1(x)}}_{f(x)} + \underbrace{\frac{\psi_2''(y)}{\psi_2(y)}}_{g(y)} + \underbrace{\frac{\psi_3''(z)}{\psi_3(z)}}_{h(z)}\right) = E$$

f, g, h must each be a const, otherwise cannot always add up to const regardless of x, y, z.

$$-\frac{\hbar^2}{2m}\frac{\psi_1''(x)}{\psi_1(x)} = E_1, \quad -\frac{\hbar^2}{2m}\frac{\psi_2''(y)}{\psi_2(y)} = E_2, \text{ etc}$$

$E_1 + E_2 + E_3 = E$ (Note: E_1, E_2, E_3 not independ'nt, must sum to E)

$$\Rightarrow \frac{d^2\psi_1(x)}{dx^2} = \frac{-2mE_1}{\hbar^2}\cdot\psi_1(x) = -k_x^2\,\psi_1(x),$$ likewise for y, z

define $k_x^2 = 2mE_1/\hbar^2$

Have broken 3D problem into 3 1D problems

(1D solution) $\Rightarrow \psi_1(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n_x\pi x}{a}\right)$

$$E_1 = \frac{n_x^2\hbar^2\pi^2}{2ma^2}, \quad n_x = 1,2,3,\ldots$$

$$\psi_2(y) = \sqrt{\ }\sin\left(\frac{n_y\pi y}{a}\right), \quad E_2 = n_y^2\left(\hbar^2\pi^2/2ma^2\right)$$

$$E_{tot} = E = E_1 + E_2 + E_3 = \underbrace{\frac{\hbar^2 \pi^2}{2ma^2}}_{\varepsilon}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$\Psi(x,y,z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi \cdot y}{a}\right) \sin\left(\frac{n_z \pi \cdot z}{a}\right)$$

States identified by 3 "quantum numbers"

(n_x, n_y, n_z) <u>all</u> ≥ 1 $\left(\begin{array}{c} n=0 \text{ not allowed} \\ \text{since} \Rightarrow \Psi = 0 \end{array}\right)$

Dirac Notation $|n_x, n_y, n_z\rangle \longleftrightarrow \Psi_{n_x n_y n_z}$

Grd state $(1,1,1)$ has energy $= 3 \cdot \frac{\hbar^2 \pi^2}{2ma^2} = 3 \cdot \varepsilon$

But there are <u>three</u> 1st-excited states $(1,1,2)$ $(1,2,1)$ $(2,1,1)$ all w/ the same energy =

$(1^2 + 1^2 + 2^2)\,\varepsilon = 6\,\varepsilon$

The 3 states are linearly independent (one state cannot be written as a linear combo of the other two)

Linearly ind. states w/ same eigenvalue are called degenerate states. (Doesn't arise in 1D, usually) Note symmetry in x, y, z in potential $V(\vec{r})$. Degenerate states often arise from symmetries.

Note can write $\hat{H} = \hat{H}_x + \hat{H}_y + \hat{H}_z$,

$\hat{H}_x = \frac{\hat{p}_x^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$, etc

$\Psi = \Psi_{n_x n_y n_z}$ is simultaneously an eigenfcn of all 4 operators $\hat{H}, \hat{H}_x, \hat{H}_y, \hat{H}_z$:

$\hat{H}\Psi = E\Psi = (n_x^2 + n_y^2 + n_z^2)\,\varepsilon\Psi$, $\hat{H}_x\Psi = E_1\Psi = n_x^2\,\varepsilon\Psi$, etc

When can two different operators have simultaneous eigenfcns? Answer (to be shown): When they <u>commute</u>

Definition: commutator of operators $\hat{A}$ and $\hat{B}$
$= [\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$ = an operator

So, 2 operators commute if their commutator is zero: $\hat{A}\hat{B} = \hat{B}\hat{A} \iff [\hat{A}, \hat{B}] = 0$

Why would we care if there are states that are simultaneously eigenfunctions of 2 operators $\hat{A}$ & $\hat{B}$?

Recall: eigenfcn of $\hat{A}$ = state of definite A
so eigenfcn of both $\hat{A}$ & $\hat{B}$ = state definite A & B

Example: $[\hat{x}, \hat{p}_x] = ?$

$$[\hat{x}, \hat{p}_x] = \hat{x}\,\hat{p}_x - \hat{p}_x\,\hat{x} = x\,\frac{\hbar}{i}\frac{\partial}{\partial x}(\ \ ) - \frac{\hbar}{i}\frac{\partial}{\partial x}\left[x\cdot(\ \ )\right]$$

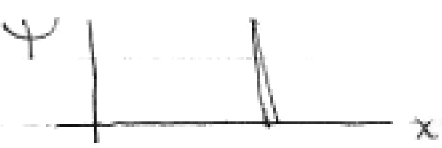
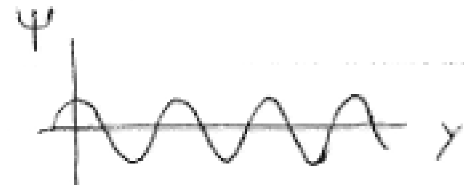
Operate on arbitrary state $f(x)$:

$$[\hat{x}, \hat{p}_x]\, f = \frac{\hbar}{i}\underbrace{\left[x\frac{\partial f}{\partial x} - \frac{\partial}{\partial x}(x\cdot f)\right]}_{\cancel{x\frac{\partial f}{\partial x}} - \cancel{x\frac{\partial f}{\partial x}} - \underbrace{\left(\frac{\partial x}{\partial x}\right)}_{1}\cdot f} = -\frac{\hbar}{i}\cdot f$$

True for <u>any</u> f $\Rightarrow$ $\boxed{[\hat{x}, \hat{p}_x] = i\hbar} = -\frac{\hbar}{i}$

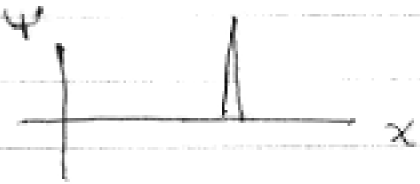
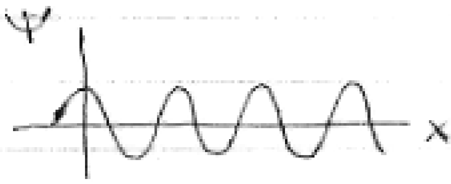
But, $[\hat{x}, \hat{y}] = 0$, $[\hat{x}, \hat{p}_y] = 0$, $[\hat{p}_x, \hat{p}_y] = 0$

So, it is possible to have a state that is simultaneously a state of definite x & definite p_y

$\Rightarrow$  AND 

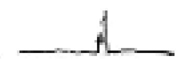
both allowed simultaneously (subject to usual caveat about non-normalizable states)

But, it is NOT possible to have simultaneous eigenstates of $\hat{x}$ and $\hat{p}_x$

 can't have both! 

This is very different from the classical situation:

x , $p_x = m v_x$ ← Can have well-defined, precise values of x AND p_x

In QM, if we start w/ a state of definite p_x ($\Psi =$ ) and we measure x, then Ψ collapses to a state of definite x ($\Psi =$ ) and the momentum information is destroyed.

Theorem: If $[\hat{A}, \hat{B}] = 0$, then there exist simultaneous eigenfns of $\hat{A}$ and $\hat{B}$:

$$\hat{A}\Psi = a\Psi \quad , \quad \hat{B}\Psi = b\Psi \quad (\text{same } \Psi)$$

Proof: Given Ψ such that $\hat{A}\Psi = a\Psi$, assume that Ψ is a non-degenerate eigenfn of $\hat{A}$. (We'll relax this condition later). Ψ = non-degenerate eigenfn of $\hat{A}$ means that only Ψ and multiples of Ψ ($= c\Psi$) are eigenfns. No other linearly independent eigenstate exist

Now, operate w/ $\hat{B}$ on both sides of $\hat{A}\Psi = a\Psi$:

$$\underbrace{\hat{B}\hat{A}\Psi} = \hat{B}a\Psi = a\hat{B}\Psi \quad \text{(since } \hat{B} \text{ is linear op.)}$$

$$\hat{A}(\hat{B}\Psi) = a(\hat{B}\Psi) \Rightarrow \hat{B}\Psi \text{ is also eigenstate of } \hat{A}$$

But assumed eigenstate of $\hat{A}$ non-degenerate $\Rightarrow$

$\hat{B}\Psi$ is a multiple of $\Psi \Rightarrow \hat{B}\Psi = b\Psi$ for some b

(Done.) So Ψ is a state of definite A (value $= a$) and a state of definite B (value $= b$)

Can be shown that (HW problem!) $\boxed{[\hat{H}, \hat{p}_x] = i\hbar \frac{\partial V}{\partial x}}$ (1D)

$\Rightarrow$ if $V = 0 =$ const (free particle), then $\partial V/\partial x = 0$,

$[\hat{H}, \hat{p}_x] = 0 \Rightarrow$ possible to have states of definite energy and definite momentum.

Easy! $\Psi(x) = A e^{i(kx - \omega t)}$

$\hat{p}\Psi = \hbar k \Psi$, $\quad \hat{H}\Psi = \left(\frac{\hbar^2 k^2}{2m}\right)\Psi$

(But only true for free particle. If any $V(x) \neq$ const present, then eigenstates of $\hat{H}$ are not $\hat{p}$ eigenstates)

Particle in a 3D box $[\hat{H}_x, \hat{H}_y] = \left(\frac{\hbar^2}{2m}\right)^2 [\hat{p}_x^2, \hat{p}_y^2] = 0$

$\Rightarrow$ states of definite $\hat{H}_x$ and $\hat{H}_y$ allowed

sure! $\Psi = \Psi_{n_x n_y n_z}$