Why are the energy eigenfunctions so important?

1) All ~~solutions~~ states can be written as a linear combination of them:

$$\Psi(x,t=0) = \psi(x) = \sum_n a_n \phi_n(x)$$

for some set of $\{a_n\}$.

2) When we write $\Psi(x,t=0)$ this way, ~~the~~ it's trivial to solve the TDSE! The solution is

$$\Psi(x,t) = \sum_n a_n \phi_n(x) e^{-i\omega_n t}$$

This tells us how ~~the~~ Ψ evolves for all time, as long as no measurements are made! ("No collapse of the wavefunction")

3) If Ψ involves only one energy eigenfunction, then the expectation values of all observables are constant in time $\Rightarrow$ they never change:

$$\langle A \rangle = \text{constant in time}$$

when $\psi(x) = \phi_n(x)$, an energy e.f.

(Proof in the homework.)

Three Additional Comments

① The spatial probability $|\Psi(x,t)|^2$ does not change in time:

when $\psi(x) = \phi_n(x)$ $\quad P(x) = |\Psi^* \Psi|^2 = \phi_n^*(x) e^{i\omega_n t} \phi_n(x) e^{-i\omega_n t} = |\phi_n(x)|^2$

(2)

(2) Stationary states are the QM analogs of systems at rest. $\Psi(x,t)$ still depends on time via $e^{-i\omega_n t}$, but everything else is constant. The phase phactor $e^{-i\omega_n t}$ is also <u>unobservable</u> in this state. (It cancels in $P(x) = \Psi^* \Psi$).

(3) <u>Question</u> ~~Since~~ we can always write

$$\Psi(x, t=\phi) = \psi(x) = \sum_n a_n \phi_n(x)$$

and all $\phi_n(x)$ are stationary, aren't all QM states stationary??

$\Rightarrow$ Answer: No! (Otherwise nothing in physics could ever change in time!)

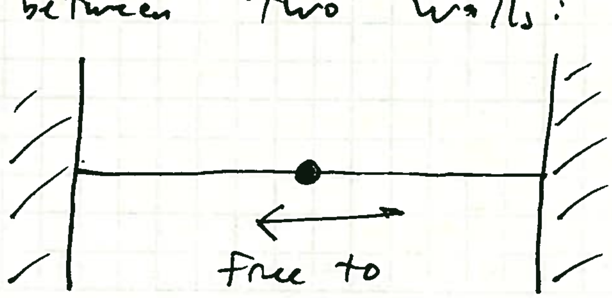
Only states which are represented by <u>one and only one</u> $\phi_n(x)$ are stationary.

4) The phase factor becomes very important in non-stationary states, because it causes interference

Suppose $\psi(x) = e^{i\alpha} \phi_1(x) + e^{i\beta} \phi_2(x)$

Then $|\psi(x)|^2 = |\phi_1(x)|^2 + |\phi_2(x)|^2 + \ldots e^{i(\beta-\alpha)} + \ldots e^{-i(\beta-\alpha)}$

<u>Particle in a Box</u> - The simplest bound states in QM. Particle on a wire (in 1-D), trapped between two walls:



This is a reasonable physical model for ~~absorption~~ a gas molecule in a 1D container or a conduction electron in

The potential is $V(x) = \begin{cases} \emptyset, & 0 < x < L \\ +\infty, & x < \emptyset, x > L \end{cases}$

We solve this problem by finding the <u>stationary states</u>.

The Hamiltonian is $\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$

For $0 < x < L$, $\hat{H} = \frac{-\hbar^2}{2m}$. In this region, the TISE reads

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\varphi(x) = E\varphi(x)$$

$$\varphi''(x) + \frac{2mE}{\hbar^2}\varphi(x) = \emptyset.$$

~~Sol~~ General Solution is

$$\varphi(x) = Ae^{ikx} + Be^{-ikx}, \quad k \equiv \frac{\sqrt{2mE}}{\hbar}$$

However, the potential $V(x)$ imposes extra <u>boundary conditions</u>. Ordinarily, we have two boundary conditions on $\psi(x)$:

1) $\psi(x)$ is continuous
2) $\frac{d\psi(x)}{dx}$ is continuous, except where $V(x) \to \infty$.

For the particle in a box, only ① applies.
So what is $\psi(x)$ outside of $\emptyset < x < L$?
If $V(x)$ were finite there, the $\psi(x)$ could be non-zero $\Rightarrow$ this is called QM tunneling.
But for the particle in a box, $\psi(x)$ must be zero outside the box, so there is no chance to find the particle outside $\emptyset < x < L$.

So we require

① $\psi(0) = \emptyset$

& ② $\psi(L) = \emptyset$.

$\therefore$ From ①, $A + B = \emptyset$

From ②, $Ae^{ikL} + Be^{-ikL} = \emptyset$

but $B = -A$, so

$$A\left(e^{ikL} - e^{-ikL}\right) = \emptyset$$

$$2A \sin kL = \emptyset$$

$$\boxed{\sin kL = \emptyset}$$ From boundary condition.

This is satisfied when

$$kL = n\pi, \quad n = \emptyset, \pm 1, \pm 2, \pm 3$$

$$k_n = \frac{n\pi}{L} \Rightarrow \boxed{E_n = \frac{\hbar^2 n^2 \pi^2}{2mL^2}} \leftarrow \text{Energy eigenvalues.}$$

The e.f. are $\phi_n(x) = A\left(e^{ikx} - e^{-ikx}\right)$

$$= 2A \sin kx = \underbrace{2A}_{\text{redefine constant } A} \sin\left(\frac{n\pi x}{L}\right)$$

energy e.f. $\longrightarrow$ $\boxed{\phi_n(x) = A \sin\left(\frac{n\pi x}{L}\right)}$

However, the solutions ~~this~~ with $n = \emptyset$ or $n < \emptyset$ are phony:

$$\psi(x) = A \sin\left(\frac{(0)\pi x}{L}\right) = \emptyset$$

particle is nowhere??!

$$\psi(x) = A \sin\left(\frac{(-n)\pi x}{L}\right) = \underbrace{A \sin\left(\frac{n\pi x}{L}\right)}$$

$(-n)$ solutions aren't unique.

So the solution is

$$\boxed{\begin{aligned} \psi_n(x) &= A \sin\left(\frac{n\pi x}{L}\right) \\ E_n &= \frac{\hbar^2 n^2 \pi^2}{2mL^2} \quad n = 1,2,3,\ldots \end{aligned}}$$

But what is A? Apply normalization condition:

$$\int_{-\infty}^{\infty} P(x)\,dx = \int_{-\infty}^{\infty} \psi^*(x)\,\psi(x)\,dx = 1$$

$$\therefore |A|^2 = \frac{2}{L}, \quad A = \sqrt{\frac{2}{L}}.$$

If $F(x)$ is periodic with period $2L$, then $f(x)$ can be written as

$$F(x) = \sum_{n=0}^{\infty} \left[A_n \cos\left(\frac{n\pi x}{L}\right) + B_n \sin\left(\frac{n\pi x}{L}\right)\right]$$

This can also be written as

$$F(x) = \sum_{n=-\infty}^{\infty} a_n e^{in\pi x/L}$$

We say the functions $\{e^{in\pi x/L}\}$ form a complete set because any periodic function can be written as a linear combination of them.

To find the coefficients $\{a_m\}$ for a particular $F(x)$, we evaluate

one integral for each coeff. $\rightarrow$ $a_m = \frac{1}{2L}\int_{-L}^{L} F(x)\, e^{im\pi x/L}\, dx$

We proved this taking advantage of the ortho-normality condition for $\{e^{in\pi x/L}\}$:

$$\frac{1}{2L}\int_{-L}^{L}\left(e^{in\pi x/L}\right)\left(e^{-im\pi x/L}\right)dx = \delta_{nm} = \begin{cases} 1, & n=m \\ \emptyset, & n\neq m. \end{cases}$$

All of this is a <u>discrete</u> Fourier Series, which is great for <u>periodic functions</u>. We can also represent non-periodic functions, using a continuous limit.

Re-write it this way:

$$F(x) = \sum_{n=-\infty}^{\infty} a_n e^{in\pi x/L} \underbrace{\Delta n}_{1} = \frac{L}{\pi} \sum_{n=-\infty}^{\infty} a_n e^{in\pi x/L} \left(\frac{\pi \Delta n}{L}\right)$$

Define $k \equiv \frac{n\pi}{L}$, $\Delta k = \frac{\pi \Delta n}{L}$ and $\frac{A(k)}{\sqrt{2\pi}} \equiv \frac{L}{\pi} a_n$.

Then

$$F(x) = \frac{1}{\sqrt{2\pi}} \sum_{k=-\infty}^{\infty} A(k) e^{ikx} \Delta k.$$

Now let $L \to \infty$, so the period becomes infinite.
Then $\Delta k \to dk$, k becomes continuous:

$$\boxed{F(x) = \frac{1}{\sqrt{2\pi}} \underbrace{\int_{-\infty}^{\infty} dk}_{\text{integral over } k} A(k) e^{ikx}}$$

Fourier Series for a non-periodic function.

$A(k)$ is the "Fourier Transform" of $F(x)$

$$\boxed{A(k) = \frac{1}{\sqrt{2\pi}} \underbrace{\int_{-\infty}^{\infty} dx}_{\text{integral over } x} F(x) e^{-ikx}}$$

"Prove via Fourier's Trick"

We put $\frac{1}{\sqrt{2\pi}}$ into the definition of $A(k)$ so that the expressions for $F(x)$ and $A(k)$ would have the same constant in front.

$A(k)$ is the analog of $\{a_n\}$ for a continuous Fourier Transform. If we insert the Fourier expression for $A(k)$ into the expression for $F(x)$ we get

$$F(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\, e^{ikx} \left[\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx'\, F(x')\, e^{-ikx'} \right]$$

use x' on RHS,

interchange the order of integration:

$$F(x) = \int_{-\infty}^{\infty} dx'\, F(x') \underbrace{\left[\frac{1}{2\pi} \int_{-\infty}^{\infty} dk\, e^{ik(x-x')} \right]}_{\delta(x-x')}$$

This looks like the definition of the Dirac Delta Function:

$$F(x) = \int_{-\infty}^{\infty} dx'\, F(x')\, \delta(x-x')$$

if

$$\delta(x-x') = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk\, e^{ik(x-x')}$$

This is one way to write the Dirac Delta Function. If we re-write it as

$$\delta(x-x') = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \left(e^{ikx}\right)\left(e^{-ikx'}\right)$$

It looks like the continuous analog of the Kronecker Delta:

& ortho-normal condition for the discrete Fourier Series.

$$\frac{1}{2L}\int_{-L}^{L}\left(e^{in\pi x/L}\right)\left(e^{-im\pi x/L}\right)dx = \delta_{mn}$$ for discrete Fourier Series,

Kronecker Delta

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} dk\left(e^{ikx}\right)\left(e^{-ikx'}\right) = \delta(x-x')$$ for continuous Fourier Transform

Dirac Delta Function.

Similiarly, the discrete functions $\{e^{in\pi x/L}\}$ are complete

for periodic $f(x)$, and the continuous functions

$\{e^{ikx}\}$ are complete for certain $f(x)$, those for which

$$\int_{-\infty}^{\infty}|f(x)|^2 dx \text{ is finite.}$$

This is extremely useful in QM, because $\int_{-\infty}^{\infty}|\psi(x)|^2 dx$

must be equal to 1 if the Born interpretation of $\psi(x)$ holds.

We solved the QM Particle in a Box.

Solution : $\phi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$

$$E_n = \frac{\hbar^2 n^2 \pi^2}{2mL^2}$$

Any intial state wave function can be written as a linear combination of the $\{\phi_n\}$:

$$\Psi(x, t=0) = \psi(x) = \sum_n a_n \phi_n$$

How do we know we can always do this? Because Fourier theory guarrantees that the functions $\left\{\sin\left(\frac{n\pi x}{L}\right)\right\}$ are complete for representing odd, periodic functions. In fact they are also ortho-normal: $\int_0^L \phi_m^*(x)\phi_n(x)\,dx = \delta_{mn}$

we use complex-conj just to prov

Kron Delt

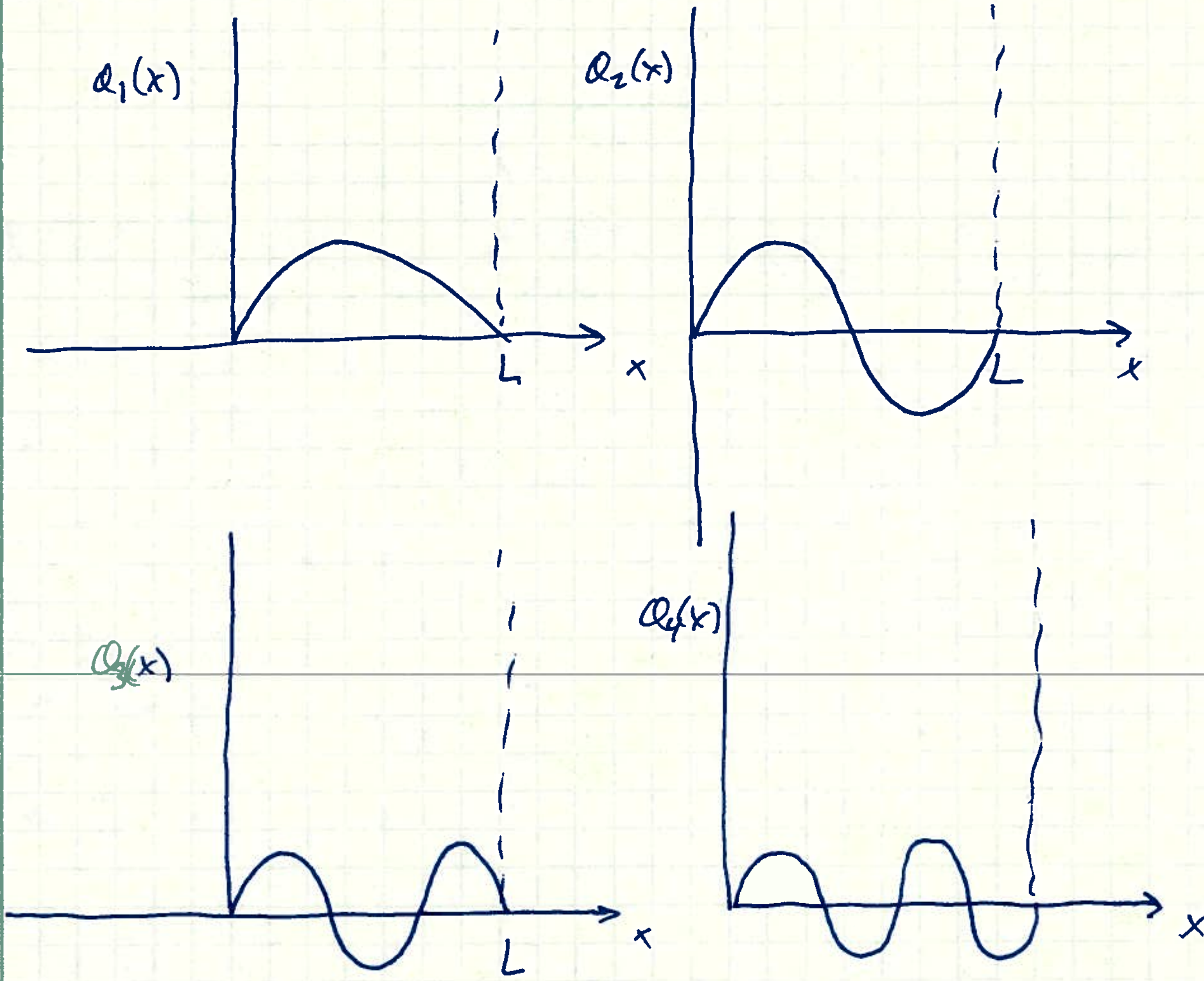
Note: $\psi(x)$ does not need to be periodic to infinity ... if fact, $\psi(x)$ is zero outside the box. We simply use the Fourier expression inside the box, and set $\psi(x) = 0$ outside:

$$\psi(x) = \begin{cases} \sum_n a_n \phi_n, & 0 < x < L \\ 0, & \text{otherwise} \end{cases}$$

Why did the particle in a box yeild sine functions as the stationary states?

Answer: because of the boundary conditions we imposed.

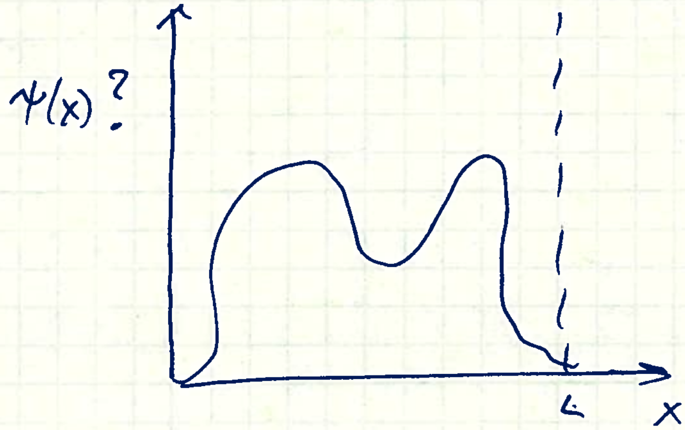
We decided that $\Psi(x)$ must go to zero at both ends of the box. This fixed the possible energy eigenfunction as "standing waves"



State (n) has (n) half sine waves.
High (n) has a large number of wiggles.
This corresponds to high energy, because

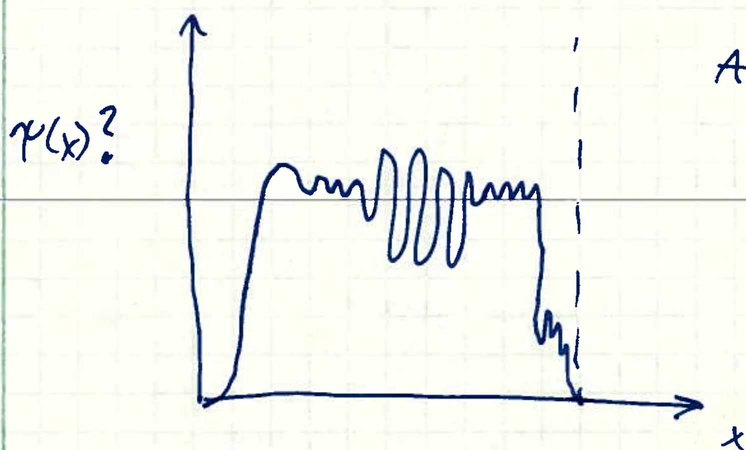
$$\hat{H} \sim \frac{d^2}{dx}$$ ← when the 2^{nd} derivative is large, the KE is high.

Question: Is this function an allowed initial state wavefunction?



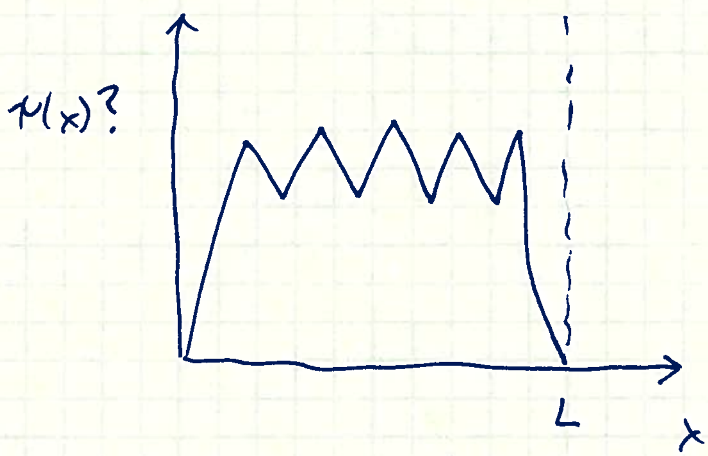
Answer: Yes! Fourier says just find the right set of $\{a_n\}$.

How about this one?



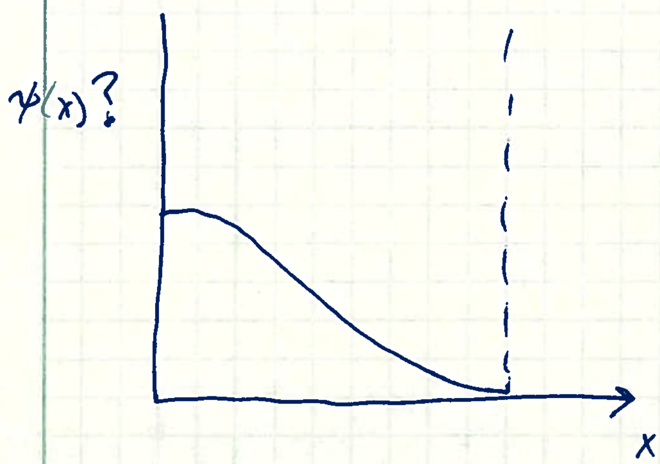
Answer: Yes!

This one?



Answer: Yes!

This one?



Answer: No! It violates the boundary condition $\psi(0) = \phi$, and a series made of sine functions cannot represent it (because $\sin(0) = \phi$ for each term).

To find the particular coefficients $\{a_n\}$ for a particular $\psi(x)$, we use "Fourier's Trick", as always:

c.c. just for practice!

$$\int \mathcal{Q}_m^*(x)\, \psi(x)\, dx = \sum_{n=1}^{\infty} a_n \underbrace{\int \mathcal{Q}_m^*(x)\, \mathcal{Q}_n(x)\, dx}$$

$$= \sum_{n=1}^{\infty} a_n \delta_{nm} \quad \text{by orthonormality}$$

$$= a_m \quad \text{since } \delta_{nm} = \phi \text{ for } n \neq m.$$

$$\therefore \boxed{a_m = \int \mathcal{Q}_m^*(x)\, \psi(x)\, dx}$$

Physical Interpretation of ~~a_n~~ $\{a_n\}$

The expansion coefficient $\{a_n\}$ have a very simple, very important physical interpretation. They represent the "amplitude" to ~~that~~ measure ~~the particular~~ a particular energy eigenvalue, where by "amplitude" we mean a complex number whose square is the probability of the measurement.

Mathematically, $\underbrace{|a_m|^2}_{\text{amplitude squared}} = P(E_m)$ = Probability to measure energy eigenvalue E_m.

We can infer this by calculating $\langle E \rangle$ for an arbitrary particle-in-a-box wavefunction:

$$\langle E \rangle = \int \psi^* \hat{H} \psi \, dx = \int \left(\sum_{n=1}^{\infty} a_n^* \phi_n^* \right) \hat{H} \left(\sum_{m=1}^{\infty} a_m \phi_m \right) dx$$

$$= \sum_n \sum_m a_n^* a_m \int \phi_n^* \underbrace{\hat{H} \phi_m}_{E_m \phi_m} dx$$

$$= \sum_n \sum_m E_m a_n^* a_m \underbrace{\int \phi_n^* \phi_m \, dx}_{\delta_{nm} \text{ by ortho-normality}}$$

$$= \sum_n \sum_m E_m \delta_{nm} (a_n^* a_m)$$

$$= \sum_n E_n a_n^* a_n$$

$$= \sum_n E_n |a_n|^2$$

But we know from the statistical definition of expectation values that for any observable,

$$\langle A \rangle = \sum_i A_i \, P(A_i)$$

Therefore we must have that $|a_n|^2 = P(E_n)$ = Probability to measure E_n

This also implies that

$\sum_n |a_n|^2 = 1 \leftarrow \{a_n\}$ should satisfy this...

The $\{a_n\}$ are similiar to $\psi(x)$ in the sense that they are both complex amplitude

- $|\psi(x)|^2 \rightarrow$ probability to observe particle with position X.
- $|a_n|^2 \rightarrow$ probability to observe particle with energy E_n.

In Schroedinger Wave Mechanics, we usually think of $\psi(x)$ as the fundamental physical quantity predicted by QM, and all other quantities as derived.

More generally, however, $\psi(x)$ is one type of amplitude which can be calculated using QM.

a_n is another type of amplitude. which can be calculated.

~~After~~

Next month we will re-cast QM ~~our notation~~ in terms of Dirac notation, which treats all of these amplitudes equally.

Free Particle – simplest Unbound State.

The ~~the~~ ~~Hamiltonian~~ Energy eigenvalue equation reads

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi(x)}{dx^2} = E\,\varphi(x) \qquad \text{Time-Independent Schroedinger Eq.}$$

$\psi(x)$: an eigenfunction of $\hat{H}$.

General Solution: $\varphi(x) = Ae^{ikx} + Be^{-ikx}$, where $k \equiv \frac{\sqrt{2mE}}{\hbar}$, so that $E = (\hbar k)^2/2m$

We got the same general solution for particle-in-the-box, but in that case the allowed values of k were restricted by the boundary condition. We found that energy eigenfunctions discrete k: $k = n\pi/L$.
For free particle, k is unrestricted, and all values are allowed.

The G.S is a sum of two momentum e.f.: e^{ikx}.
One term represents (+) ~~mom~~ p, one term represents (−) p. Since $E = \frac{p^2}{2m} = \frac{(\hbar k)^2}{2m}$, both (+) p and (−) are e.f. of $\hat{H}$. We can write

$$\varphi(x) = Ae^{ikx},$$ keeping in mind that k could be (+) or (−). (We will return to this question later.)

The strange thing is that this $\psi(x)$ cannot be normalized:

$$\int_{-\infty}^{\infty} \varphi^*\varphi\, dx = \int_{-\infty}^{\infty} |A|^2 dx \to \infty.$$

This reflects the fact that in the real world we never have a perfect plane wave which extends to infinity in all directions.

We can deal with the normalization in two ways:

1) Re-interpret $\psi(x)$ as being proportional to particle beam intensity: number of particles/second for example. Then relative beam intensities can be calculated. $\Longrightarrow$ Scattering Theory.

2) Create a normalizable single particle wave function by adding together a range of e^{ikx}:

$$\Psi(x,t=0) = \psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{ikx} dk$$

For some $\phi(k)$. This is the Fourier Transform of $\psi(x)$, and from Fourier theory we know that we can invert the expression:

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x) e^{-ikx} dx$$

Fourier Theory also tells us that:

1) Any reasonably localized $\psi(x)$ can be written in this way $\Longrightarrow$ $\{e^{ikx}\}$ are complete

2) $\{e^{ikx}\}$ are also ~~orthogonal~~ ortho-normal:

$$\int_{-\infty}^{\infty} \left(e^{ikx}\right)\left(e^{-ik'x}\right) dk = \int_{-\infty}^{\infty} e^{i(k-k')x} dx = \delta(k-k')$$

Dirac Delta Funct.

For the particle-in-a-box, we found that the expansion coefficients $\{a_n\}$ represented the amplitudes to measure a particular energy eigenvalue.

For a free particle, we have a continuum of energy eigenfunctions with a continuum of energy eigenvalues $\left(\frac{\hbar^2 k^2}{2m}\right)$. The expansion coefficients $\phi(k)$ is also continuous, and $|\phi(k)|^2 dk$ can be interpreted as the probability to measure momentum between k and $k+dk$.

Comparison of Particle-in-Box & Free Particle.

	Particle in Box	Free Particle
	bound-state	unbound-state
Energy e.f.	$\varphi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$	$\varphi = A e^{ikx} = \frac{1}{\sqrt{2\pi}} e^{ikx}$
Energy e.v.	$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$	$E_k = \frac{\hbar^2 k^2}{2m}$
	Discrete e.v. & e.f.	Continuous e.v. & e.f.
Completeness Statement	$\Psi(x,t=0) = \sum_n a_n \varphi_n$	$\Psi(x,t=0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{-ikx} dk$
Ortho-normality	$\int_0^L \varphi_m^* \varphi_n \, dx = \delta_{mn}$	$\int_{-\infty}^{\infty} e^{-i(k-k')x} dx = \delta(k-k')$
Interpretation	a_n = amplitude to measure $E=E_n$	$\phi(k)$ = amplitude to measure $p=\hbar k$

To get the fully time dependent wave function, we simply tack-on the appropriate phase factor as before:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k)\, e^{+ikx}\, e^{-iEt/\hbar}\, dk$$

or substituting $E = \hbar^2 k^2/2m$, for a free particle.

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k)\, e^{i(kx - \hbar k^2 t/2m)}\, dk.$$

$\Rightarrow$ Given the initial state $\Psi(x,t=0) = \psi(x)$, we can find $\phi(k)$.

Because $\phi(k)$ can be interpreted as a probability amplitude to observe momentum $= \hbar k$, we call it "the wave function in momentum space".

In fact, by substituting the above $\Psi(x,t)$ into the time dependent Schrodinger Eq, we can prove that $\phi(k)$ satisfies its own wave equation

Define $\Phi(k,t) = \phi(k)\, e^{-i\hbar k^2 t/2m}$

Then the TDSE for $\Phi(k,t)$ is

$$\boxed{i\hbar \frac{\partial \Phi(k,t)}{\partial t} = \frac{p^2}{2m} \Phi(k,t)}$$

"The Schrodinger Eq. in momentum Space"

for a free particle

In fact, we can re-write all of QM in p-space:

	x-space	p-space
wavefunction	$\Psi(x,t)$, $\psi(x)$	$\Phi(k,t)$, $\phi(k)$
$\hat{x}$	x	$-i\hbar \frac{d}{dp}$
$\hat{p}$	$-i\hbar \frac{d}{dx}$	p
Equation of Motion	$i\hbar \frac{\partial \Psi}{\partial t} = \left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\Psi$	$i\hbar \frac{\partial \Phi}{\partial t} = \frac{p^2}{2m} + V\left(i\hbar \frac{d}{dp}\right)\Phi$

Often we choose to work in x-space rather than p-space, although in some cases p-space makes things simpler (like the free particle.).

In most cases our preference for x-space follows from our experience with Classical Mechanics. Sometimes its easier to guess the correct Hamiltonian in x-space.