

# Chapter 12

## Wave Mechanics

P. J. Grandinetti

Chem. 4300

## Wave Function in Position & Wavenumber Representation

In quantum mechanics, we associate wavenumber with particle momentum

$$\vec{p} = \hbar \vec{k}$$

Remember the Fourier transform relation for waves?

$$c(k, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x, t) e^{-ikx} dx \quad \text{and} \quad \Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} c(k, t) e^{ikx} dk$$

Let's replace  $k$  with  $p$  in the Fourier expansions...

# Wave Function in Position and Momentum Representation

Wave function in position and momentum representations become

$$\Phi(p, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Psi(x, t) e^{-ipx/\hbar} dx.$$

and

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Phi(p, t) e^{ipx/\hbar} dp,$$

We'll use these expressions to predict a particle's properties from its wave function.

# Operators in Quantum Mechanics

## Position Operators, $\hat{x}$

Mean particle position, or expectation value of  $x$ , is weighted average calculated from wave function

$$\langle x(t) \rangle = \int_{-\infty}^{\infty} x p(x) dx = \int_{-\infty}^{\infty} x \underbrace{\Psi^*(x, t)\Psi(x, t)}_{p(x)} dx$$

In QM, we define  $\hat{x}$  operator:

$$\hat{x} \Psi(x, t) = x \Psi(x, t)$$

$\hat{x}$  operates on  $\Psi(x, t)$  to give back position times wave function.

In formalism of quantum mechanics, we write  $\langle x(t) \rangle$  as

$$\langle x(t) \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t) \hat{x} \Psi(x, t) dx = \int_{-\infty}^{\infty} \Psi^*(x, t) x \Psi(x, t) dx = \int_{-\infty}^{\infty} x \underbrace{\Psi^*(x, t)\Psi(x, t)}_{p(x)} dx$$

## Position Operators, $\hat{x}$

Other mean or expectation value quantities, such as  $\langle x^2(t) \rangle$ , are written

$$\langle x^2(t) \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t) \hat{x}^2 \Psi(x, t) dx = \int_{-\infty}^{\infty} \Psi^*(x, t) x^2 \Psi(x, t) dx = \int_{-\infty}^{\infty} x^2 \underbrace{\Psi^*(x, t) \Psi(x, t)}_{p(x)} dx$$

For any function of  $x$  we write

$$\langle f(x, t) \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t) \hat{f}(x, t) \Psi(x, t) dx = \int_{-\infty}^{\infty} \Psi^*(x, t) f(x, t) \Psi(x, t) dx = \int_{-\infty}^{\infty} f(x, t) \underbrace{\Psi^*(x, t) \Psi(x, t)}_{p(x)} dx$$

As long as the operator  $\hat{f}(x, t)$  depends only on  $x$  and  $t$ , then

$$\hat{f}(x, t) \Psi(x, t) = f(x, t) \Psi(x, t)$$

What's the point of introducing these extra steps with  $\hat{x}$ ?

## Momentum Operators, $\hat{p}$

What about mean or expectation value of particle momentum?

Using wave function in momentum basis  $\Phi(p, t)$  we calculate

$$\langle p(t) \rangle = \int_{-\infty}^{\infty} \Phi^*(p, t) \hat{p} \Phi(p, t) dp = \int_{-\infty}^{\infty} \Phi^*(p, t) p \Phi(p, t) dp = \int_{-\infty}^{\infty} p \underbrace{\Phi^*(p, t) \Phi(p, t)}_{p(p)} dp$$

Here  $\hat{p}$  operates on  $\Phi(p, t)$  to give

$$\hat{p} \Phi(p, t) = p \Phi(p, t)$$

Similarly we have

$$\langle p^2(t) \rangle = \int_{-\infty}^{\infty} \Phi^*(p, t) \hat{p}^2 \Phi(p, t) dp$$

and

$$\langle f(p, t) \rangle = \int_{-\infty}^{\infty} \Phi^*(p, t) \hat{f}(p, t) \Phi(p, t) dp$$

Again, what's the point of introducing these extra steps with  $\hat{p}$ ? Let's consider this further.

## Momentum Operators

If  $\hat{p}$  operates on  $\Psi(x, t)$  we should get same result as  $\hat{p}$  acting on  $\Phi(p, t)$

$$\langle p(t) \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t) \hat{p} \Psi(x, t) dx, \quad \text{but what is } \hat{p} \Psi(x, t) = ??$$

Use Fourier transform to expand  $\Psi(x, t)$  in momentum representation

$$\hat{p} \Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \hat{p} \Phi(p, t) e^{ipx/\hbar} dp$$

Take derivative of Fourier expansion for  $\Psi(x, t)$

$$\text{if } \Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Phi(p, t) e^{ipx/\hbar} dp \quad \text{then}$$

$$\frac{\partial}{\partial x} \Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \left( \frac{ip}{\hbar} \right) \Phi(p, t) e^{ipx/\hbar} dp = \left( \frac{i}{\hbar} \right) \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} p \Phi(p, t) e^{ipx/\hbar} dp = \left( \frac{i}{\hbar} \right) \hat{p} \Psi(x, t)$$

$$\frac{\partial}{\partial x} \Psi(x, t) = \left( \frac{i}{\hbar} \right) \hat{p} \Psi(x, t)$$



## Momentum Operators

Rearrange and find that  $\hat{p}\Psi(x, t)$  is given by

$$\hat{p}\Psi(x, t) = -i\hbar\frac{\partial}{\partial x}\Psi(x, t)$$

Identify *momentum operator* when applied to wave function in position basis as

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}$$

Operator notation allows us to work with  $\Psi(x, t)$  basis only and obtain expectation values for both  $\hat{x}$  and  $\hat{p}$ .

### Homework

Determine *position operator* when applied to wave function in momentum basis.

## Eigenfunctions and Eigenvalues

Whenever operator acts on wave function and gives back numerical value times original wavefunction then that wave function is an *eigenfunction* for that operator and numerical value returned is called the *eigenvalue*.

$$\hat{A}f(\dots) = af(\dots)$$

$f(\dots)$  is eigenfunction of  $\hat{A}$  and  $a$  is eigenvalue.

- Is  $\Psi(x, t)$  eigenfunction for  $\hat{x}$ ?  $\hat{x}\Psi(x, t) = x\Psi(x, t)$ , Yes
- Is  $\Phi(p, t)$  eigenfunction for  $\hat{p}$ ?  $\hat{p}\Phi(p, t) = p\Phi(p, t)$ , Yes
- Is  $\Psi(x, t)$  eigenfunction for  $\hat{p}$ ?  $\hat{p}\Psi(x, t) = -i\hbar\frac{d\Psi(x, t)}{dx}$ , No
- Is  $\Phi(p, t)$  eigenfunction for  $\hat{x}$ ? No. Prove this at home.

# Operators in Quantum Mechanics must be linear

Can only lead to linear differential equations involving  $\Psi$

$$\hat{A} (c_1\Psi_1 + c_2\Psi_2) = c_1\hat{A}\Psi_1 + c_2\hat{A}\Psi_2.$$

Nonlinear operations, such as

- take square root
- log
- cosine
- sine
- raise to a power—other than 0 or 1

are not allowed.

# Uncertainty and Commutator Relations

## Commutation Relations

Operators may not commute, i.e., order that operators are applied matters.

### Example

What is result when operator below is applied to a wave function?

$$\hat{x}\hat{p} - \hat{p}\hat{x} = ?$$

Hint: not zero

Recall  $\hat{p} = -i\hbar \frac{\partial}{\partial x}$ . Apply this difference operator to  $\Psi(x, t)$  we find

$$\begin{aligned}(\hat{x}\hat{p} - \hat{p}\hat{x})\Psi(x, t) &= \hat{x}\hat{p}\Psi(x, t) - \hat{p}\hat{x}\Psi(x, t) = \left(-i\hbar x \frac{\partial\Psi(x, t)}{\partial x}\right) - \left(-i\hbar \frac{\partial}{\partial x}(x\Psi(x, t))\right) \\ &= -i\hbar x \frac{\partial\Psi(x, t)}{\partial x} - \left(-i\hbar\Psi(x, t) - i\hbar x \frac{\partial\Psi(x, t)}{\partial x}\right) = i\hbar\Psi(x, t) \\ (\hat{x}\hat{p} - \hat{p}\hat{x})\Psi(x, t) &= i\hbar\Psi(x, t)\end{aligned}$$

## Commutation Relations

$$(\hat{x}\hat{p} - \hat{p}\hat{x})\Psi(x, t) = i\hbar\Psi(x, t)$$

Such operator product differences occur often in quantum mechanics. So often it is called a *commutator* and given shorthand notation

$$\hat{x}\hat{p} - \hat{p}\hat{x} = [\hat{x}, \hat{p}] = i\hbar, \quad \text{for all } \Psi(x, t)$$

When

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \neq 0$$

we say that  $\hat{A}$  and  $\hat{B}$  do not commute.

Why are commutation relations useful?

## Uncertainty and Commutator Relations

From  $[\hat{x}, \hat{p}] = i\hbar$  we obtain the uncertainty relation:  $\langle \Delta x \rangle \langle \Delta p \rangle \geq \hbar/2$

Commutator gives us more general uncertainty relationships.

$$\text{Given } [\hat{A}, \hat{B}] = iC, \text{ then } \langle \Delta A \rangle \langle \Delta B \rangle \geq \langle C \rangle / 2$$

where

$$\langle \Delta A \rangle = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$$

This general relation,  $\langle \Delta A \rangle \langle \Delta B \rangle \geq \langle C \rangle / 2$ , quantifies ability to specify precisely and simultaneously two observables for  $\hat{A}$  and  $\hat{B}$ .

# Kinetic and Potential Energy Operators



## Kinetic and Potential Energy Operators

*Kinetic energy operator* in momentum and position bases are

$$\hat{K} = \frac{\hat{p}^2}{2m} \quad \text{and} \quad \hat{K} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

- Potential energy operator,  $\hat{V}(x)$ , depend on system under study.
- Solving Schrödinger Eq. is easy or impossible depending on  $\hat{V}(x)$ .
- Examples of some easy ones are...
  - ▶ Electron trapped in 1D box of length  $L$  has potential energy operator

$$\begin{aligned}\hat{V}(x) &= 0 && \text{if } 0 \leq x \leq L, \\ \hat{V}(x) &= \infty && \text{if } x < 0 \text{ and } x > L\end{aligned}$$

This is called the *infinite well potential*.

- ▶ 1D harmonic oscillator with force constant  $\kappa_f$  has potential energy operator

$$\hat{V}(x) = \frac{1}{2} \kappa_f \hat{x}^2$$

## Total Energy Operator $\equiv$ Hamiltonian Operator

Total energy operator is sum of kinetic and potential energy operators,

$$\hat{H} = \hat{K} + \hat{V} = \frac{\hat{p}^2}{2m} + \hat{V}(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x)$$

$\hat{H}$  is called *Hamiltonian operator*. Recall Schrödinger equation

$$E\Psi(x, t) = \underbrace{\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x) \right]}_{\hat{H}} \Psi(x, t) = i\hbar \frac{\partial}{\partial t} \Psi(x, t)$$

We can write Schrödinger equation more compactly as

$$E\Psi(x, t) = \hat{H}\Psi(x, t) = i\hbar \frac{\partial}{\partial t} \Psi(x, t)$$

With this substitution we see that  $\hat{H}$  is also given by

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

# Solving the Schrödinger Equation

## Solving the Schrödinger Equation

If potential energy operator,  $\hat{V}(x)$ , depends only on position and not time then separation of variables can be used

$$\Psi(x, t) = \psi(x)\phi(t)$$

Substituting into Schrödinger equation gives

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

Dividing both sides by  $\Psi(x, t) = \psi(x)\phi(t)$  leads to

$$\underbrace{\frac{1}{\psi(x)} \left[ -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + \hat{V}(x) \psi(x) \right]}_{\text{depends only on } x} = \underbrace{i\hbar \frac{1}{\phi(t)} \frac{\partial \phi(t)}{\partial t}}_{\text{depends on } t} = E$$

For equality to remain true for all  $x$  and  $t$  both sides must equal separation constant,  $E$ , which we'll find is total energy and is time independent.

# Solving the Schrödinger Equation

This gives 2 uncoupled ODEs:

$$\frac{d\phi(t)}{dt} + \frac{iE}{\hbar} \phi(t) = 0$$

and

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} (E - \hat{V}(x)) \psi(x) = 0$$

- ODE for  $\phi(t)$  has trivial solution:  $\phi(t) = e^{-iEt/\hbar}$
- Solution to full partial differentiation equation is

$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar}$$

- Called *stationary state* as probability density is time independent,

$$|\Psi(x, t)|^2 = [\psi^*(x)e^{iEt/\hbar}] [\psi(x)e^{-iEt/\hbar}] = \psi^*(x)\psi(x)$$

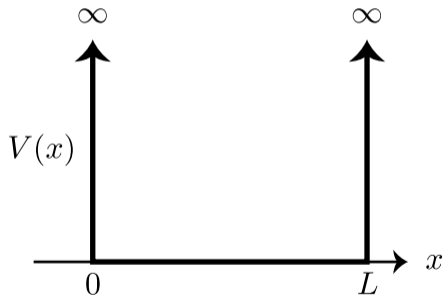
- Operator expectation values for stationary states are time independent.

- ODE for  $\psi(x)$  is called the *time independent Schrödinger equation*.
- Wave equation for  $\psi(x)$  doesn't contain  $i = \sqrt{-1}$ , so its solutions are real functions.

## Particle in Infinite Well – Stationary States

Solutions to Schrödinger equation for particle in infinite square well are analogous to string standing waves. Potential takes form

$$\hat{V}(x) = \begin{cases} 0 & \text{if } 0 \leq x \leq L \\ \infty & \text{otherwise} \end{cases}$$



Outside the well we have  $\Psi(x, t) = 0$ .

What are the stationary states,  $\Psi(x, t)$ , inside the well?

## Particle in Infinite Well – Stationary States

What are stationary states inside well?

Look for solutions to time independent Schrödinger equation,

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + \hat{V}(x)\psi(x) = E\psi(x) \quad \text{or} \quad \frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0$$

where

$$k^2 = \frac{2mE}{\hbar^2}$$

We've seen this ODE and boundary conditions before. Its solutions look like

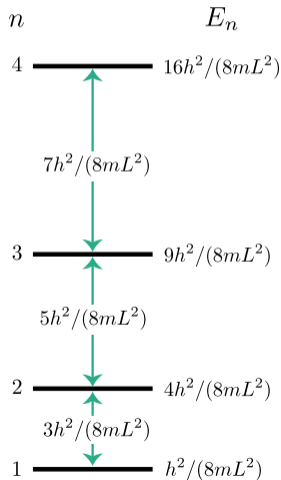
$$\psi_n(x) = B \sin k_n x \quad \text{where} \quad k_n = \frac{n\pi}{L} \quad \text{and} \quad n = 1, 2, 3, \dots$$

In this case we have

$$k_n^2 = \frac{n^2\pi^2}{L^2} = \frac{2mE_n}{\hbar^2} \quad \text{or} \quad \boxed{E_n = \frac{n^2\hbar^2}{8mL^2}} \leftarrow \text{Stationary State Energies}$$

# Particle in Infinite Well – Stationary States

## Stationary State Energies



- In quantum mechanics we describe  $n$  as a *principal quantum number*.
- On the right are energy levels and spacing for  $n = 1$  to 4,
- Note lowest energy is not zero.
- Lowest possible energy is  $E_1 = h^2/(8mL^2)$ .
- Every bound quantum particle has *zero point energy*. This is consequence of particle's wave properties.
- Energy level spacings are not equal and increase with increasing  $n$ .



## Particle in Infinite Well – Stationary States

For wave function to give probability density function, it has to be normalized:

$$\int_0^L |\psi_n(x)|^2 dx = B^2 \int_0^L \sin^2 \frac{n\pi}{L} x dx = B^2 \left( \frac{x}{2} - \frac{L}{4n\pi} \sin \frac{2n\pi x}{L} \right) \Big|_0^L = B^2 \left( \frac{L}{2} \right) = 1$$

which leads to  $B = \sqrt{2/L}$ .

Normalized wave functions are given by,

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x$$

Any wave function inside infinite well potential can be expressed as linear combination of these stationary states

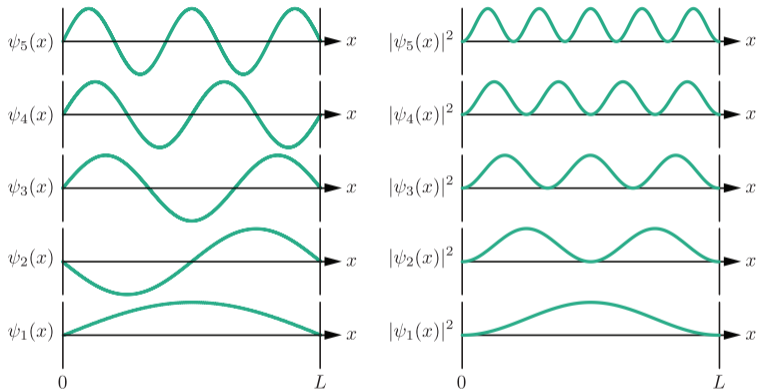
$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) \phi_n(t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi}{L} x \right) e^{-iE_n t/\hbar}$$

## Probability of observing a particle in an infinite well

# Position Measurement of Particle in Infinite Well

Wave function magnitude squared is probability density.

Zero chance of finding particle at nodes where amplitude is always zero.



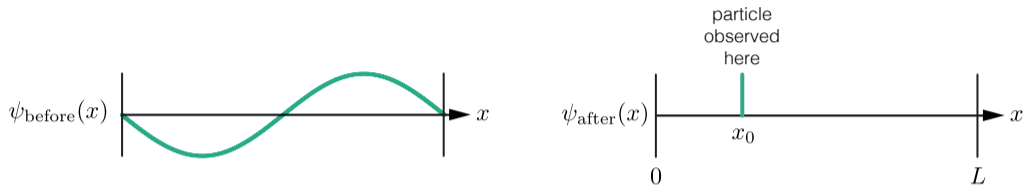
Left are first 5 wave functions for particle in infinite square well.

Right are corresponding probability densities.

Doesn't mean particle cannot have well defined position. We can easily measure its position.

# Collapsing Wave Function with a Measurement

Act of measuring particle's position changes wave function.



Immediately after position measurement wave function would be

$$\psi_{\text{after}}(x) = \delta(x - x_0) = \sum_{n=1}^{\infty} c_n \psi_n(x)$$

In practice, particle located within measurement spatial resolution :  $\Delta x$ .

Better wave function description after measurement could be

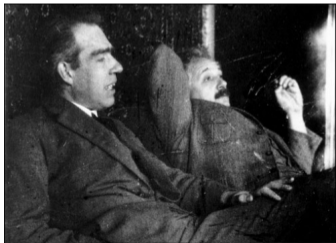
$$\psi_{\text{after}}(x) = \begin{cases} 1/\sqrt{\Delta x} & \text{for } -\Delta x/2 < x < \Delta x/2 \\ 0 & \text{otherwise} \end{cases}$$

Act of measurement *collapses wave function* to wave packet centered on spot where particle is found.

## Collapsing Wave Function with a Measurement

Can we always predict where particle will be found in position measurement? **No.**

- Every time you measure particle's position it appears at random positions consistent with its wave function in box.
- No one has ever figured out how to predict exactly where particle will be found in given measurement.
- It's always random and no one knows why.
- Einstein didn't like this and famously said "God doesn't play dice."



To which Niels Bohr replied "Don't tell God what to do."

## Predicting Measurement Outcomes

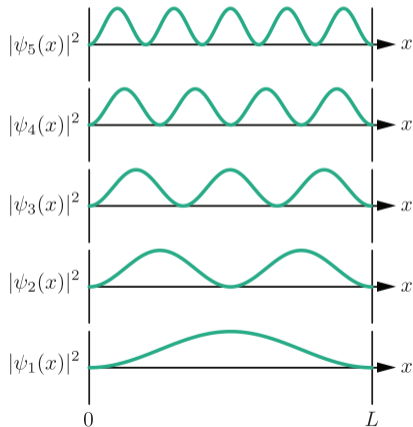
While outcome of given measurement will be random, wave function does give us precise probability for where particle will be observed.

For example, if particle in infinite well has  $n = 2$  stationary state wave function,

$$\psi_2(x) = \sqrt{\frac{2}{L}} \sin \frac{2\pi}{L}x$$

then...

- we're 100% certain that particle will never be observed at  $x = L/2$ .
- if we measured its kinetic energy we would also be 100% certain that we would obtain  $E_2 = 4h^2/(8mL^2)$



# Predicting Measurement Outcomes

## Example

What is probability of locating particle in 1D infinite well between  $L/4$  and  $3L/4$  when particle is in  $n = 1$  stationary state?

$$\text{Probability} = \int_{L/4}^{3L/4} |\psi_1(x)|^2 dx = \frac{2}{L} \int_{L/4}^{3L/4} \sin^2 \frac{\pi}{L} x dx = \frac{2}{L} \left( \frac{x}{2} - \frac{L}{4\pi} \sin \frac{2\pi}{L} x \right) \Big|_{L/4}^{3L/4}$$

$$\text{Probability} = \frac{1}{2} + \frac{1}{\pi} \approx 0.82$$

## Momentum Measurement of Stationary State

- If we operate on stationary state of particle in 1D infinite well with  $\hat{p}$ ,

$$\hat{p}\psi_n(x) = -i\hbar \frac{\partial}{\partial x} \left( \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L}x \right) = -i\hbar \sqrt{\frac{2}{L}} \left( \frac{n\pi}{L} \right) \cos \frac{n\pi}{L}x$$

we find that  $\psi_n(x)$  are NOT eigenstates of  $\hat{p}$ .

- If we calculate

$$\langle p \rangle = \int_0^L \psi_n^*(x) \hat{p} \psi_n(x) dx$$

we get  $\langle p \rangle = 0$ .

- How can average momentum,  $\langle p \rangle$ , be zero when kinetic energy,  $E_n = \frac{n^2 \hbar^2}{8mL^2}$ , is non-zero?
- Makes more sense to rewrite  $\psi_n(x)$  as

$$\psi_n(x) = \sqrt{\frac{2}{L}} \left( \frac{e^{ikx} - e^{-ikx}}{2i} \right) \quad \leftarrow 2 \text{ traveling waves going in opposite directions.}$$



## Momentum Measurement of Stationary State

If we apply  $\hat{p}$  to

$$\psi_n(x) = \sqrt{\frac{2}{L}} \left( \frac{e^{ikx} - e^{-ikx}}{2i} \right)$$

we find

$$\begin{aligned} \hat{p}\psi_n(x) &= \sqrt{\frac{2}{L}} \left[ \left( -i\hbar \frac{\partial}{\partial x} \right) \left( \frac{e^{ikx}}{2i} \right) - \left( -i\hbar \frac{\partial}{\partial x} \right) \left( \frac{e^{-ikx}}{2i} \right) \right] \\ &= \sqrt{\frac{2}{L}} \left[ \underbrace{\left( -\hbar k_n \right) \left( \frac{e^{ikx}}{2i} \right)}_{\textcircled{1}} - \underbrace{\left( +\hbar k_n \right) \left( \frac{e^{-ikx}}{2i} \right)}_{\textcircled{2}} \right] \end{aligned}$$

① eigenstate of  $\hat{p}$  with eigenvalue of  $-\hbar k_n$  is **right** traveling wave

② eigenstate of  $\hat{p}$  with eigenvalue of  $+\hbar k_n$  is **left** traveling wave.

- Think of 1D well stationary states as 2 traveling waves with opposite signs of momenta,  $\pm\hbar k_n$ .
- Any real wave function, i.e., no imaginary part, describes state with no net motion. Why?

# Hermitian Operators

# Hermitian Operators

Expectation values associated with physically observable quantities,

$$\text{physical observables must be real (not complex)} \longrightarrow \langle O \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{O} \Psi dx$$

While  $\langle O \rangle$  must be real, i.e.,  $\langle O \rangle = \langle O \rangle^*$ , or

$$\int_{-\infty}^{\infty} \Psi^* \hat{O} \Psi dx = \left[ \int_{-\infty}^{\infty} \Psi^* \hat{O} \Psi dx \right]^*$$

both  $\Psi$  and  $\hat{O}$  can be complex. Since  $(z_1 z_2 z_3)^* = z_1^* z_2^* z_3^*$ , we rewrite right hand side as

$$\int_{-\infty}^{\infty} \Psi^* (\hat{O} \Psi) dx = \left[ \int_{-\infty}^{\infty} \Psi^* \hat{O} \Psi dx \right]^* = \int_{-\infty}^{\infty} \Psi \hat{O}^* \Psi^* dx = \int_{-\infty}^{\infty} \Psi (\hat{O} \Psi)^* dx = \int_{-\infty}^{\infty} (\hat{O} \Psi)^* \Psi dx$$

Define *Hermitian operator* as one that satisfies a more general (and stronger) condition:

$$\boxed{\int_{-\infty}^{\infty} \Psi_1^* (\hat{O} \Psi_2) dx = \int_{-\infty}^{\infty} (\hat{O} \Psi_1)^* \Psi_2 dx}$$

Operator associated with physically observable quantities must be *hermitian*.

# Hermitian Operators

## Example

Is  $\hat{D} = \partial/\partial x$  is a hermitian operator?

$$\text{Check if } \int_{-\infty}^{\infty} \Psi_1^* (\hat{D}\Psi_2) dx \stackrel{?}{=} \int_{-\infty}^{\infty} (\hat{D}\Psi_1)^* \Psi_2 dx \quad \text{or} \quad \int_{-\infty}^{\infty} \Psi_1^* \left( \frac{\partial\Psi_2}{\partial x} \right) dx \stackrel{?}{=} \int_{-\infty}^{\infty} \left( \frac{\partial\Psi_1}{\partial x} \right)^* \Psi_2 dx$$

Use integration by parts

$$\int u dv = uv - \int v du,$$

take  $u = \Psi_1^*$  with  $du = \frac{\partial\Psi_1^*}{\partial x} dx$  and  $v = \Psi_2$  with  $dv = \frac{\partial\Psi_2}{\partial x} dx$ .

$$\int_{-\infty}^{\infty} \Psi_1^* \frac{\partial\Psi_2}{\partial x} dx = \Psi_1^* \Psi_2 \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \Psi_2 \frac{\partial\Psi_1^*}{\partial x} dx$$

# Hermitian Operators

## Example

Is  $\hat{D} = \partial/\partial x$  is a hermitian operator?

$$\text{Check if } \int_{-\infty}^{\infty} \Psi_1^* \left( \frac{\partial \Psi_2}{\partial x} \right) dx \stackrel{?}{=} \int_{-\infty}^{\infty} \left( \frac{\partial \Psi_1}{\partial x} \right)^* \Psi_2 dx$$

$$\int_{-\infty}^{\infty} \Psi_1^* \frac{\partial \Psi_2}{\partial x} dx = \cancel{\Psi_1^* \Psi_2} \Big|_{-\infty}^{\infty} \overset{0}{\rightarrow} - \int_{-\infty}^{\infty} \Psi_2 \frac{\partial \Psi_1^*}{\partial x} dx$$

1st term on right goes to zero as all wave functions should at  $\pm\infty$ .

We are left with

$$\int_{-\infty}^{\infty} \Psi_1^* \left( \frac{\partial \Psi_2}{\partial x} \right) dx = - \int_{-\infty}^{\infty} \left( \frac{\partial \Psi_1}{\partial x} \right)^* \Psi_2 dx$$

Right hand side has opposite sign of left hand side.

We conclude that  $\hat{D} = \partial/\partial x$  is NOT a hermitian operator.

## Hermitian adjoint of an operator

For any operator,  $\hat{A}$ , (not necessarily hermitian) we define its *hermitian adjoint*,  $\hat{A}^\dagger$ , with

$$\int \Psi_1^* \hat{A}^\dagger \Psi_2 dx = \int (\hat{A} \Psi_1)^* \Psi_2 dx$$

- In previous example we saw that  $\hat{D} = \partial/\partial x$  and  $\hat{D}^\dagger = -\partial/\partial x$ .
- Any operator equal to its hermitian adjoint is a hermitian operator, e.g.  $\hat{p}^\dagger = \hat{p}$ .
- Other helpful theorems about adjoints are
  - ▶ Adjoint of sum of 2 operators equals sum of their adjoints:  $(\hat{A} + \hat{B})^\dagger = \hat{A}^\dagger + \hat{B}^\dagger$
  - ▶ Sum of 2 hermitian operators is a hermitian operator.
  - ▶ Even if  $\hat{A}$  is not hermitian we find that both  $\hat{A} + \hat{A}^\dagger$  and  $i(\hat{A} - \hat{A}^\dagger)$  are hermitian.
  - ▶ Given arbitrary operators  $\hat{A}$  and  $\hat{B}$  we have  $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$

# Eigenfunctions of Hermitian Operators are Orthogonal

If  $\psi_m(x)$  and  $\psi_n(x)$  are eigenfunctions of a hermitian operator then

$$\int_{-\infty}^{\infty} \psi_m^*(x) \psi_n(x) dx = \delta_{m,n}$$

where  $\delta_{m,n}$  is *Kronecker delta function*:

$$\delta_{mn} = \begin{cases} 0 & \text{if } m \neq n \\ 1 & \text{if } m = n \end{cases}$$

## Web Video: Double Slit Experiment