Wave Mechanics

Chapter 11

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Wave Function in Position & Wavenumber Representation

Remember the Fourier transform relation for waves?

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

In quantum mechanics we associate wavenumber with particle momentum

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

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

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

and

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

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

Operators in Quantum Mechanics

Position Operators, $\hat{x}$

Mean particle position is weighted average calculated from wave function

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

In formalism of quantum mechanics we write this as

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

$\hat{x}$ is the position operator.

Position Operators, $\hat{x}$

When $\hat{x}$ operates on $\Psi(x,t)$ we obtain trivial result,

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

Operation returns the position times wave function.

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

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

where $\hat{x}^2 = \hat{x}\cdot\hat{x}$ and

$$\hat{x}^2\,\Psi(x,t) = x^2\Psi(x,t)$$

For any function of x we write

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

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

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

Momentum Operators, $\hat{p}$

What about mean momentum of particle?

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

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

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

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

All this seems obvious—hardly merits introduction of operator notation.

But let's consider this a little further.

Momentum Operators

$\hat{p}$ acting on $\Psi(x,t)$ should give same result as $\hat{p}$ acting on $\Phi(p,t)$

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

But what happens when $\hat{p}$ operates on $\Psi(x,t)$?

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

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

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

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

Momentum Operators

Rearrange

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

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* applied to wave function in position basis is

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

Homework

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

Linear Operators

Any operation on wave function in quantum mechanics must be linear, e.g.,

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

Nonlinear operations, such as take square root, log, cosine, sine, raise to a power–other than 0 or 1, are not allowed.

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*.

$$\hat{A} f(\ldots) = a f(\ldots)$$

$f(\ldots)$ 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 $\Psi(x,t)$ is an eigenfunction for $\hat{p}$? $\hat{p}\Psi(x,t) = -i\hbar\frac{d\Psi(x,t)}{dx}$, no
- Is $\Phi(p,t)$ is not eigenfunction for $\hat{x}$? No, you prove it!

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

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

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

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

When $[\hat{A},\hat{B}] = 0$ we say that $\hat{A}$ and $\hat{B}$ commute.

We just proved that $\hat{x}$ and $\hat{p}$ do not commute and that

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

Uncertainty and Commutator Relations

Recall $\langle \Delta x \rangle \langle \Delta p \rangle \geq \hbar/2$?

Commutator gives us more general uncertainty relationships. Given

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

where

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

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

Kinetic and Potential Energy Operators

Kinetic energy operator in momentum and position bases are

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

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

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

  This is called the *infinite well potential*.

- 1D harmonic oscillator with force constant κ_f has potential energy operator

$$\hat{V}(x) = -\frac{1}{2}\kappa_\text{f}\hat{x}^2$$

Total Energy = Hamiltonian Operator

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

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

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

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

We can write Schrödinger equation as

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

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

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

Solving the Schrödinger Equation

Time Independent 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

$$-\frac{\hbar^2}{2m}\phi(t)\frac{\partial^2\psi(x)}{\partial x^2} + \phi(t)\hat{V}(x)\psi(x) = i\hbar\psi(x)\frac{\partial\phi(t)}{\partial t}$$

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

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

Right hand side depends only on t. Left hand side depends only on x.

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.

Time Independent Schrödinger Equation

This gives 2 uncoupled ODEs:

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

and

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

2nd ODE for $\psi(x)$ is called the *time independent Schrödinger equation*.

Note that wave equation for $\psi(x)$ doesn't contain $i = \sqrt{-1}$ so its solutions are real functions.

Stationary States

Since ODE for $\phi(t)$ has trivial solution

$$\phi(t) = e^{-iEt/\hbar}$$

then solution to full time dependent Schrödinger equation can be written

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

This is called *stationary state* as probability density is time independent,

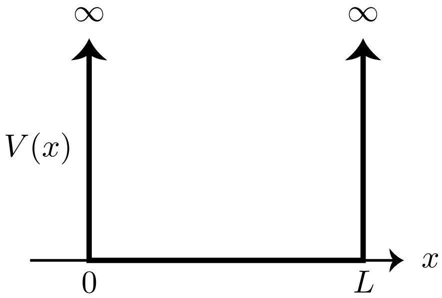
$$|\Psi(x,t)|^2 = \left[\psi^*(x)e^{iEt/\hbar}\right]\left[\psi(x)e^{-iEt/\hbar}\right] = \psi^*(x)\psi(x)$$

All operator expectation values are time independent for stationary states.

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

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



Outside the well we have $\psi(x) = 0$.

What are the stationary states inside the well?

Particle in Infinite Well – Stationary States

What are stationary states inside well?

Look for solutions to time independent Schrödinger equation,

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

where

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

We've seen this ODE before and know that its solutions look like

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

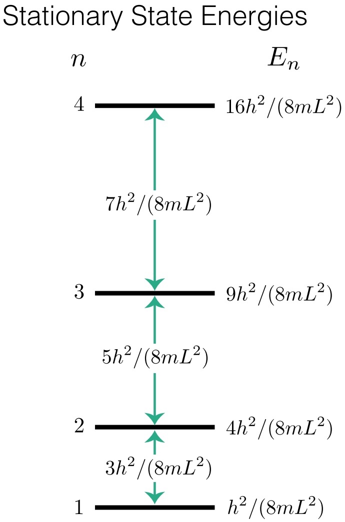
In this case we have

$$k_n^2 = \frac{n^2\pi^2}{L^2} = \frac{2mE_n}{\hbar^2} \qquad \text{or} \qquad \boxed{E_n = \frac{n^2h^2}{8mL^2}}$$

Particle in Infinite Well – Stationary States

In quantum mechanics we describe n as a *principal quantum number*.

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

To normalize wave function

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

which leads to $B = \sqrt{2/L}$.
Stationary states given by,

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

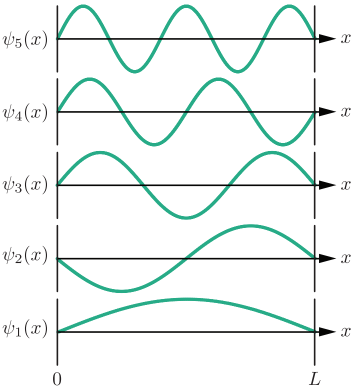
Any wave function inside infinite well potential can be expressed as linear combination of these stationary states

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

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.

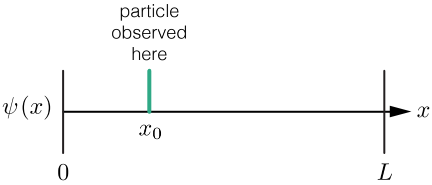
Right are corresponding probability densities.

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

$$\psi_{\text{after}}(x) = \delta(x - x_0)$$

In practice particle located within measurement spatial resolution : Δa.
Better wave function description after measurement could be

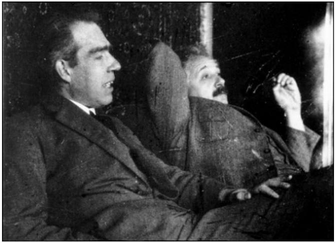
$$\psi_{\text{after}}(x) = \begin{cases} 1/\sqrt{\Delta a} & \text{for } -\Delta a/2 < x < \Delta a/2 \\ 0 & \text{otherwise} \end{cases}$$

We say that act of measurement *collapses the wave function* to wave packet centered on spot where particle is found.

Collapsing Wave Function with a Measurement

Can we 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."

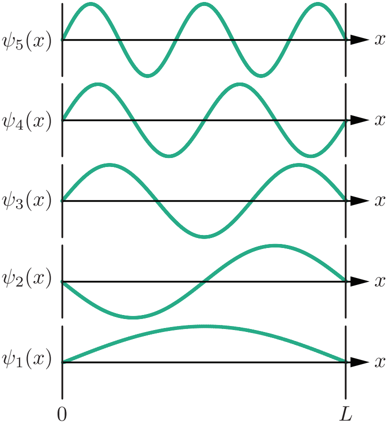
Predicting Measurement Outcomes

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

e.g., 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 $x = L/2$.



Similarly, 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?

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

$$= \frac{2}{L} \left(\frac{x}{2} - \frac{L}{4\pi} \sin \frac{2\pi}{L} x \right) \Big|_{L/4}^{3L/4} = \frac{1}{2} + \frac{1}{\pi}$$

$$\approx 0.82$$

Web Video: Double Slit Experiment

Momentum Measurement of Stationary State

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

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

Stationary states, $\psi_n(x)$, are not eigenstates of $\hat{p}$.

Calculate

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

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

How can momentum be zero when kinetic energy, $E_n = \frac{n^2h^2}{8mL^2}$, is non-zero?

Makes more sense to rewrite $\psi_n(x)$ as

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

Momentum Measurement of Stationary State

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

Wave function is 2 traveling waves going in opposite directions.

If we apply $\hat{p}$ to $\psi_n(x)$ written in this form we find

$$\hat{p}\psi_n(x) = \sqrt{\frac{2}{L}}\left[\left(-i\hbar\frac{\partial}{\partial x}\right)\left(\frac{e^{ikx}}{2i}\right) - \left(-i\hbar\frac{\partial}{\partial x}\right)\left(\frac{e^{-ikx}}{2i}\right)\right]$$

$$= \sqrt{\frac{2}{L}}\Bigg[\underbrace{\left(-\hbar k_n\right)\left(\frac{e^{ikx}}{2i}\right)}_{①} - \underbrace{\left(+\hbar k_n\right)\left(\frac{e^{-ikx}}{2i}\right)}_{②}\Bigg]$$

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

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

Momentum Measurement of Stationary State

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

Each stationary states in 1D well can be thought as traveling waves with equal but opposite momenta of magnitude $|\hbar k_n|$.

Any real wave function—that is, no imaginary part—describes a state with no net motion. Can you explain why?

Hermitian Operators

Expectation values associated with physically observable quantities,

$$\langle O \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi dx$$

must be real (not complex).

While $\langle O \rangle$ must be real, both Ψ and $\hat{A}$ can be complex.

For integral to be real we require $\hat{A}$ to be *hermitian operator*:

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

Since $(z_1 z_2 z_3)^* = z_1^* z_2^* z_3^*$ we rewrite right hand side as

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

Define hermitian operator as one that satisfies

$$\boxed{\int_{-\infty}^{\infty} \Psi_1^* \left(\hat{A} \Psi_2 \right) dx = \int_{-\infty}^{\infty} \left(\hat{A} \Psi_1 \right)^* \Psi_2 \, dx}$$

Hermitian Operators

Example

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

We need to check if

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

Start with left hand side of equation and use integration by parts

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

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

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

Hermitian Operators

Example

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

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

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 of this equation has opposite sign of right hand side of

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

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

Hermitian adjoint of an operator

For any operator (not necessarily hermitian) we define its *hermitian adjoint*

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

From previous example you see that $\hat{D} = \partial/\partial x$ and $\hat{D}^\dagger = -\partial/\partial x$.
Any operator equal to its hermitian adjoint is hermitian, e.g. $\hat{p}^\dagger = \hat{p}$.
Other helpful theorems about adjoints are

- Adjoint of sum of 2 operators equals sum of their adjoints:

  $$\left(\hat{A} + \hat{B}\right)^\dagger = \hat{A}^\dagger + \hat{B}^\dagger$$

  Similarly, sum of 2 hermitian operators is hermitian.
- Although $\hat{A}$ is not hermitian we find that

  both $\hat{A} + \hat{A}^\dagger$ and $i\left(\hat{A} + \hat{A}^\dagger\right)$ are hermitian.
- Given 2 arbitrary operators $\hat{A}$ and $\hat{B}$ we have

  $$\left(\hat{A}\hat{B}\right)^\dagger = \hat{B}^\dagger \hat{A}^\dagger$$

Eigenfunctions of Hermitian Operators are Orthogonal

If $\psi_m(x)$ and $\psi_n(x)$ are eigenfunctions of a hermitian operator, say $\hat{A}$, then

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

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

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