

Week 2

The Schrödinger Equation

2.1 Ehrenfest Theorem and Uncertainty Principle

1/8:

- Announcement: PSet 1 due Friday at midnight.
- Recap.
 - $\psi(\vec{r}, t)$ is a wave function to which we associate a **probability density**.
 - Integrating this probability density over a volume yields the probability that the particle is in V .
 - Moreover, ψ is not arbitrary but must satisfy the Schrödinger equation.
 - \hat{p} is the momentum operator, defined as the differential operator $-i\hbar\vec{\nabla}$.
 - Expressing the Schrödinger equation in terms of \hat{p} , we see that it represents the application of a Hamiltonian operator in the usual form from last quarter (i.e., kinetic plus potential energy) to a certain function.
 - $\langle\hat{r}\rangle$ is the mean position, and $\langle\hat{p}\rangle$ is the mean momentum.
 - The mean position and mean momentum satisfy the classical relation, i.e., $d\langle\hat{r}\rangle/dt = \langle\hat{p}\rangle/m$.
- **Probability density:** The quantity given as follows. *Given by*

$$|\psi(\vec{r}, t)|^2$$

- We now prove something even more amazing than the classical relation result: An analogy to the classical Newton's law.
- **Ehrenfest's theorem:** The time derivative of the expectation value of the momentum operator is related to the expectation value of the force $F := -\vec{\nabla}V$ on a massive particle moving in a scalar potential $V(\vec{r}, t)$ as follows.

$$\frac{d\langle\hat{p}\rangle}{dt} = \langle-\vec{\nabla}V(\vec{r}, t)\rangle$$

Proof. Consider the Schrödinger equation:

$$-i\hbar\frac{\partial\psi}{\partial t} = \frac{\hbar^2}{2m}\vec{\nabla}^2\psi - V(\vec{r}, t)\psi$$

Take the complex conjugate of it. This means that we're sending $i \mapsto -i$, keeping V fixed (it's real), and sending $\psi \mapsto \psi^*$ (the inclusion of i in the Schrödinger equation means that ψ is complex in general and thus has a nontrivial complex conjugate).

$$-i\hbar\frac{\partial\psi^*}{\partial t} = -\frac{\hbar^2}{2m}\vec{\nabla}^2\psi^* + V(\vec{r}, t)\psi^*$$

Also observe that

$$\int d^3\vec{r} \psi^* \vec{\nabla}(\vec{\nabla}^2\psi) = \int d^3\vec{r} \vec{\nabla} \cdot [\psi^* \vec{\nabla}^2\psi] - \int d^3\vec{r} \vec{\nabla}\psi^* \vec{\nabla}^2\psi = - \int d^3\vec{r} \vec{\nabla}\psi^* \vec{\nabla}^2\psi$$

where the first term goes to zero by the divergence theorem and the boundary condition. (See PSet 1, Q2a for a full explanation of this zeroing out.) Similarly, we have that

$$\int d^3\vec{r} \vec{\nabla}\psi^* \vec{\nabla}(\vec{\nabla}\psi) = - \int d^3\vec{r} \vec{\nabla}^2\psi^* \vec{\nabla}\psi$$

This means that altogether,

$$\begin{aligned} \int d^3\vec{r} \psi^* \vec{\nabla}^3\psi &= \int d^3\vec{r} \vec{\nabla}^2\psi^* \vec{\nabla}\psi \\ \int d^3\vec{r} [\vec{\nabla}^2\psi^* \vec{\nabla}\psi - \psi^* \vec{\nabla}^3\psi] &= 0 \end{aligned}$$

We will now use the two Schrödinger substitutions and the above equation to substitute into the following algebraic derivation.

$$\begin{aligned} \frac{d\langle \hat{p} \rangle}{dt} &= \frac{d}{dt} \left(\int d^3\vec{r} \psi^* (-i\hbar \vec{\nabla}\psi) \right) \\ &= \int d^3\vec{r} \frac{\partial \psi^*}{\partial t} (-i\hbar \vec{\nabla}\psi) + \int d^3\vec{r} \psi^* \left(-i\hbar \vec{\nabla} \frac{\partial \psi}{\partial t} \right) \\ &= \int d^3\vec{r} \left(-i\hbar \frac{\partial \psi^*}{\partial t} \right) (\vec{\nabla}\psi) + \int d^3\vec{r} \psi^* \vec{\nabla} \left(-i\hbar \frac{\partial \psi}{\partial t} \right) \\ &= \int d^3\vec{r} \left(-\frac{\hbar^2}{2m} \vec{\nabla}^2\psi^* + V(\vec{r}, t)\psi^* \right) (\vec{\nabla}\psi) \\ &\quad + \int d^3\vec{r} \psi^* \vec{\nabla} \left(\frac{\hbar^2}{2m} \vec{\nabla}^2\psi - V(\vec{r}, t)\psi \right) \\ &= \int d^3\vec{r} \left[-\frac{\hbar^2}{2m} \vec{\nabla}^2\psi^* (\vec{\nabla}\psi) \right] + \int d^3\vec{r} \psi^* \vec{\nabla} \left(\frac{\hbar^2}{2m} \vec{\nabla}^2\psi \right) \\ &\quad + \int d^3\vec{r} \left[V(\vec{r}, t)\psi^* (\vec{\nabla}\psi) + \psi^* \vec{\nabla} [-V(\vec{r}, t)\psi] \right] \\ &= \int d^3\vec{r} -\frac{\hbar^2}{2m} \left[\vec{\nabla}^2\psi^* (\vec{\nabla}\psi) - \psi^* \vec{\nabla}^3\psi \right] \\ &\quad + \int d^3\vec{r} \left[V(\vec{r}, t)\psi^* (\vec{\nabla}\psi) - \psi^* \vec{\nabla} [V(\vec{r}, t)\psi] - \psi^* V(\vec{r}, t) (\vec{\nabla}\psi) \right] \\ &= \int d^3\vec{r} \psi^* (-\vec{\nabla} V(\vec{r}, t)) \psi \\ &= \langle -\vec{\nabla} V(\vec{r}, t) \rangle \end{aligned}$$

as desired. □

- In quantum mechanics, we have **observables** which are in one-to-one correspondence with operators.

Observables	Operators (\hat{O})
\vec{r}	$\hat{\vec{r}}$
$V(\vec{r}, t)$	$\hat{V}(\vec{r}, t)$
$\hat{\vec{p}}$	$-i\hbar \vec{\nabla}$
\hat{H}	$-\frac{\hbar^2}{2m} \vec{\nabla}^2 + V(\vec{r}, t)$

Table 2.1: Observables vs. operators.

- Recall that any Hermitian operator has a real observable.

- Define

$$\hat{O}_{ij} := \int d^3\vec{r} \psi_i^* \hat{O} \psi_j$$

- Then note that

$$\hat{O}_{ij} = (\hat{O}_{ji})^*$$

- Thus, an equivalent definition of a Hermitian operator is one such that the above equation is satisfied for all relevant i, j .

- Recall that the Schrödinger equation is linear.

- Let $\psi = \sum_i c_i \psi_i$.

- Then

$$\int d^3\vec{r} \psi^* \hat{O} \psi = \sum_{i,j} \int d^3\vec{r} c_i^* \psi_i^* \hat{O} c_j \psi_j = \sum_{i,j} c_i^* c_j \hat{O}_{ij}$$

is real.

- Takeaway: Averages over arbitrary wavefunctions are real.
- Similarly, suppose that \vec{r} is Hermitian. Then any function $V(\vec{r})$ of it is also Hermitian.
- For example, the momentum operator is a Hermitian operator:

$$\int d^3\vec{r} \psi_i^* (-i\hbar \vec{\nabla} \psi_j) = \left(\int d^3\vec{r} \psi_j^* (-i\hbar \vec{\nabla} \psi_i) \right)^* = \int d^3\vec{r} \psi_j (i\hbar \vec{\nabla} \psi_i^*) \rightarrow - \int d^3\vec{r} \vec{\nabla} \psi_j (i\hbar \psi_i^*)$$

- To prove the leftmost equality above, we can use integration by parts as follows.

$$\begin{aligned} \int d^3\vec{r} \psi_j (i\hbar \vec{\nabla} \psi_i^*) &= i\hbar \int d^3\vec{r} \vec{\nabla} (\psi_j \psi_i^*) - \int d^3\vec{r} \vec{\nabla} \psi_j (i\hbar \psi_i^*) \\ &= i\hbar \vec{\nabla} \int d^3\vec{r} (\psi_j \psi_i^*) - \int d^3\vec{r} \vec{\nabla} \psi_j (i\hbar \psi_i^*) \\ &= i\hbar \vec{\nabla} 0 - \int d^3\vec{r} \vec{\nabla} \psi_j (i\hbar \psi_i^*) \\ &= - \int d^3\vec{r} \vec{\nabla} \psi_j (i\hbar \psi_i^*) \end{aligned}$$

- Note that the left integral above goes to zero because of the boundary condition.
- This is relevant to PSet 1, Q2a!

- Linear algebra analogy.

- Recall that we can write any vector \vec{v} componentwise as $\vec{v} = v_x \vec{x} + v_y \vec{y} + v_z \vec{z}$.
- We can apply matrices A to such vectors to generate other vectors via $A\vec{v} = \vec{v}'$ and the like.
- Lastly, we have an inner product \cdot such that $\vec{a} \cdot \vec{b} = \delta_{ab}$, where $a, b = x, y, z$.
- On an infinite-dimensional vector space, such as that containing all the ψ , we still can decompose $\psi = \sum_n c_n \psi_n$ into an infinite sum of basis components, apply operators $\hat{O}\psi = \psi'$, and have an inner product $\int d^3\vec{r} \psi_m^* \psi_n = \delta_{mn}$.
- Another analogy: Like the inner product of a vector and unit vector is the component of the vector in that direction (e.g., $\vec{v} \cdot \vec{x} = v_x$), we have

$$\int d^3\vec{r} \psi_m^* \psi = \int d^3\vec{r} \psi_m^* \sum_n c_n \psi_n = c_m$$

- One more analogy: $\vec{x}^T A \vec{x} = A_{xx}$ is like $\langle \psi_i | \hat{O} | \psi_i \rangle = \hat{O}_{ii}$.

2.2 Time-Independent Potentials

1/10:

- Recap of important equations.
 - Momentum and Hamiltonian operators.
 - Schrödinger equation.
 - Expectation values of \vec{x} and \vec{p} , the classical relation between them, and Ehrenfest's theorem.
 - Hermitian operator condition.
 - The fact that their observables are real.
 - Examples: \hat{p} , \hat{H} , $\hat{p}^2/2m$, $V(\vec{r}, t)$.

- **Adjoint** (of \hat{O}): The operator defined according to the following rule. Denoted by \hat{O}^\dagger . Constraint

$$\int d^3\vec{r} \psi_i^* \hat{O} \psi_j = \int d^3\vec{r} (\hat{O}^\dagger \psi_i)^* \psi_j$$

- A self-adjoint (Hermitian) operator is an operator satisfying $\hat{O} = \hat{O}^\dagger$.
- Dirac notation.
 - Associate with each $\psi(\vec{r}, t)$ a “ket” $|\psi\rangle$ and a “bra” $\langle\psi|$.
 - These are like vectors.
 - The full “bra-ket” $\langle\psi_i|\psi_j\rangle := \int d^3\vec{r} \psi_i^* \psi_j$.
 - We also have $\langle\psi_i|\hat{O}|\psi_j\rangle := \int d^3\vec{r} \psi_i^* \hat{O} \psi_j$.
 - Essentially, we're just representing this Hilbert-space integral inner product in typical inner product notation!
- The condition for an operator being Hermitian/self-adjoint in Dirac notation:

$$\langle\psi_i|\hat{O}|\psi_j\rangle = \langle\psi_i|\hat{O}\psi_j\rangle = \langle\hat{O}^\dagger\psi_i|\psi_j\rangle$$

- We also have that

$$\langle\psi_i|\hat{O}_1\hat{O}_2|\psi_j\rangle = \langle\psi_i|\hat{O}_1\hat{O}_2\psi_j\rangle = \langle\hat{O}_1^\dagger\psi_i|\hat{O}_2\psi_j\rangle = \langle\hat{O}_2^\dagger\hat{O}_1^\dagger\psi_i|\psi_j\rangle$$

- This is very relevant to PSet 1, Q3a!
- Dirac notation allows us to represent complicated expressions such as

$$\int d^3\vec{r} \psi'^* \psi = \left(\int d^3\vec{r} \psi^* \psi' \right)^*$$

in the form

$$\langle\psi|\psi'\rangle = (\langle\psi'|\psi\rangle)^*$$

- In Dirac notation, the Hermitian condition becomes

$$\langle\psi_i|\hat{O}_1\hat{O}_2\psi_j\rangle = \langle\hat{O}_2\hat{O}_1\psi_i|\psi_j\rangle$$

- We also have that

$$\langle\psi_i|\hat{O}_1\hat{O}_2\psi_j\rangle = \left(\langle\psi_j|\hat{O}_2\hat{O}_1\psi_i\rangle \right)^*$$

- This is also relevant to PSet 1, Q3a!
- This last statement has some consequences.

- In particular, if $\psi_i = \psi_j = \psi$, then

$$\langle \psi | \hat{O}_1 \hat{O}_2 \psi \rangle = \left(\langle \psi | \hat{O}_2 \hat{O}_1 \psi \rangle \right)^*$$

- Thus, by adding and subtracting the quantities in the above result, we learn that

$$\langle \psi | (\hat{O}_1 \hat{O}_2 - \hat{O}_2 \hat{O}_1) \psi \rangle$$

is an imaginary number and

$$\langle \psi | (\hat{O}_1 \hat{O}_2 + \hat{O}_2 \hat{O}_1) \psi \rangle$$

is a real number.

- Example: The commutator of the position and momentum operators gives a purely imaginary number.

- We have that

$$[\hat{p}_x, \hat{x}]f = (\hat{p}_x x - x \hat{p}_x)f = -i\hbar \frac{\partial}{\partial x}(xf) + xi\hbar \frac{\partial f}{\partial x} = -i\hbar \frac{\partial x}{\partial x}f - i\hbar x \frac{\partial f}{\partial x} + i\hbar x \frac{\partial f}{\partial x} = -i\hbar f$$

- Thus,

$$[\hat{p}_x, \hat{x}] = -i\hbar$$

as desired.

- Can ψ_n be an eigenstate of \hat{O}_1 and \hat{O}_2 simultaneously?

- In the mold of a typical eigenvalue equation $A\vec{x}_n = \lambda_n \vec{x}_n$, let

$$\hat{O}\psi_n = O_n\psi_n \qquad \hat{O}_1\psi_n = O_{1,n}\psi_n \qquad \hat{O}_2\psi'_m = O_{2,m}\psi'_m$$

- Then we have that

$$\begin{aligned} \hat{O}_1\psi_n &= O_{1,n}\psi_n \\ \hat{O}_2\hat{O}_1\psi_n &= O_{1,n}\hat{O}_2\psi_n = O_{1,n}O_{2,n}\psi_n \end{aligned}$$

and

$$\begin{aligned} \hat{O}_2\psi_n &= O_{2,n}\psi_n \\ \hat{O}_1\hat{O}_2\psi_n &= O_{2,n}\hat{O}_1\psi_n = O_{2,n}O_{1,n}\psi_n \end{aligned}$$

- These are the relevant constraints.

- If such a ψ_n exists, then we can determine the values of \hat{O}_1, \hat{O}_2 simultaneously to infinite precision.

- The commutator is associated with a compatible observable.

- In particular, when two operators commute, we say that the associated physical observables are **compatible**.

- Because waves move in a **wave packet**, there is some uncertainty in the position.

- In particular, the uncertainty of \hat{A} in a given state ψ is

$$\langle \psi | (\hat{A} - \langle \hat{A} \rangle)^2 | \psi \rangle$$

- An alternate form of this expression is

$$\langle \psi | \langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2 | \psi \rangle$$

■ Wagner proves this as in MathChapter B from CHEM26100Notes.

- **Wave packet:** It is a continuous sum of waves of different frequencies.
- If ψ_n is an eigenstate of \hat{A} ...

– Then

$$\langle \psi_n | \hat{A} | \psi_n \rangle = A_n \langle \psi_n | \psi_n \rangle = A_n$$

– Similarly,

$$\langle \psi_n | \hat{A}^2 | \psi_n \rangle = A_n^2 \langle \psi_n | \psi_n \rangle = A_n^2$$

– Therefore, the uncertainty of \hat{A} in an eigenstate is $A_n^2 - (A_n)^2 = 0$.

- Note that the condition “ ψ is an eigenstate of \hat{A} ” can be denoted via $\hat{A} |\psi_n\rangle = A_n |\psi_n\rangle$.

- **Heisenberg uncertainty principle.** *Given by*

$$\sigma_x \sigma_{p_x} \geq \frac{\hbar}{2}$$

- Why is this the case? It is related to $[p_x, x] = -i\hbar$.

– The full derivation is in the notes (transcribed below), but for now, know that it is a general fact that

$$\sigma_A^2 \sigma_B^2 \geq \frac{1}{4} |\langle \psi | [A, B] | \psi \rangle|^2$$

– We demonstrate this via the **Schwarz inequality**.

– One thing is always complex; the other is always real.

- **Cauchy-Schwarz inequality.** *Given by*

$$(f, f)(g, g) \geq |(f, g)|^2$$

– (f, g) denotes the inner product of f and g , where f, g are elements of an abstract vector space.

- **Schwarz inequality.** *Given by*

$$\left(\int d^3\vec{r} |f|^2 \right) \left(\int d^3\vec{r} |g|^2 \right) \geq \left| \int d^3\vec{r} f g^* \right|^2$$

– In Dirac’s notation, this is

$$\langle f | f \rangle \cdot \langle g | g \rangle \geq |\langle f | g \rangle|^2$$

- Full derivation of the Heisenberg uncertainty principle.

– Apply the Schwarz inequality to $f = (\hat{A} - \langle \hat{A} \rangle) \psi$ and $g = (\hat{B} - \langle \hat{B} \rangle) \psi$, for \hat{A}, \hat{B} Hermitian.

– Recall that the following identities hold for Hermitian/self-adjoint operators.

$$\langle \psi | \hat{A} | \psi' \rangle = \langle \psi | \hat{A} \psi' \rangle = \langle \hat{A} \psi | \psi' \rangle \quad \langle \psi | \hat{A}^2 | \psi' \rangle = \langle \hat{A} \psi | \hat{A} \psi' \rangle$$

– Consequently, we have that

$$\begin{aligned} \sigma_A^2 \cdot \sigma_B^2 &= \langle \psi | (\hat{A} - \langle \hat{A} \rangle)^2 | \psi \rangle \cdot \langle \psi | (\hat{B} - \langle \hat{B} \rangle)^2 | \psi \rangle \\ &= \langle (\hat{A} - \langle \hat{A} \rangle) \psi | (\hat{A} - \langle \hat{A} \rangle) \psi \rangle \cdot \langle (\hat{B} - \langle \hat{B} \rangle) \psi | (\hat{B} - \langle \hat{B} \rangle) \psi \rangle \\ &\geq \left| \langle (\hat{A} - \langle \hat{A} \rangle) \psi | (\hat{B} - \langle \hat{B} \rangle) \psi \rangle \right|^2 \\ &= \left| \langle \psi | \underbrace{(\hat{A} - \langle \hat{A} \rangle)}_{\Delta \hat{A}} \underbrace{(\hat{B} - \langle \hat{B} \rangle)}_{\Delta \hat{B}} | \psi \rangle \right|^2 \end{aligned}$$

Now, any product of operators can be expressed as one half of the sum of the **commutator** and the **anticommutator**. Thus, continuing,

$$\begin{aligned} &= \left| \langle \psi | \frac{1}{2} ([\Delta \hat{A}, \Delta \hat{B}] + \{\Delta \hat{A}, \Delta \hat{B}\}) | \psi \rangle \right|^2 \\ &= \frac{1}{4} \left| \langle \psi | [\Delta \hat{A}, \Delta \hat{B}] + \{\Delta \hat{A}, \Delta \hat{B}\} | \psi \rangle \right|^2 \end{aligned}$$

Recall from above that the mean value of the commutator is an imaginary number and the mean value of the anticommutator is a real number. Thus, if we split the above equation into two terms, the mean value of the anticommutator will be squared, hence a positive number that we can get rid of and maintain the inequality. Lastly, we can compute that $[\Delta \hat{A}, \Delta \hat{B}] = [\hat{A}, \hat{B}]$. Therefore,

$$\geq \frac{1}{4} \left| \langle \psi | [\hat{A}, \hat{B}] | \psi \rangle \right|^2$$

- Example: Since $[p_x, x] = -i\hbar$, we can recover the Heisenberg uncertainty principle from the above inequality.
- There's some stuff in the notes that is very relevant to PSet 1, Q3b.

- **Commutator** (of \hat{O}_1, \hat{O}_2): The operator defined as follows. *Denoted by $[\hat{O}_1, \hat{O}_2]$. Given by*

$$[\hat{O}_1, \hat{O}_2] = \hat{O}_1 \hat{O}_2 - \hat{O}_2 \hat{O}_1$$

- **Anticommutator** (of \hat{O}_1, \hat{O}_2): The operator defined as follows. *Denoted by $\{\hat{O}_1, \hat{O}_2\}$. Given by*

$$\{\hat{O}_1, \hat{O}_2\} = \hat{O}_1 \hat{O}_2 + \hat{O}_2 \hat{O}_1$$

2.3 Office Hours (Matt)

- PSet 1, Q2a: Conceptual reason why the first term in the integration by parts vanishes?
 - Boundary conditions in each of the three directional integrals.
- Quite heavily attended, but Matt still got around.

2.4 Discussion Section

- There's not that much content to go over today, so we'll talk about some more mathematical tools like the Dirac delta function and Fourier transforms.
- **Dirac delta function:** The function defined as follows. *Denoted by $\delta(\mathbf{x} - \mathbf{x}_0)$. Given by*

$$\delta(x - x_0) = \begin{cases} \infty & x = x_0 \\ 0 & x \neq x_0 \end{cases}$$

- Useful for solving the Schrödinger equation; this is a potential that we'll solve for.
- Important application:

$$\int_a^b dx \delta(x - x_0) f(x) = \begin{cases} f(x_0) & x_0 \in [a, b] \\ 0 & \text{otherwise} \end{cases}$$

- Examples.

1.

$$\int_{-5}^5 dx \delta(x+4)(x^2 - 3x + 4) = x^2 - 3x + 4 \Big|_{x=-4} = 32$$

2.

$$\int_0^\infty \delta(x + \pi) \cos(x) = 0$$

– Because $x_0 = -\pi \notin [0, \infty)$.

- Defining a notion of equality.

– Let $D_1(x), D_2(x)$ be functions of the δ -function.

■ Example: $D_1(x) = \delta(x+3)e^{-3x^2}$.

– We say that $D_1(x) = D_2(x)$ if

$$\int_{-\infty}^{\infty} dx D_1(x) f(x) = \int_{-\infty}^{\infty} dx D_2(x) f(x)$$

for any smooth function f .

- δ -function equalities.

1. $x\delta(x) = 0$.

2. $\delta(x) = \delta(-x)$.

3. $\delta(cx) = \frac{1}{|c|}\delta(x)$.

4. $\int_{-\infty}^{\infty} dx \delta(a-x)\delta(x-b) = \delta(a-b)$.

5. $g(x)\delta(x-a) = g(a)\delta(x-a)$.

- These equalities will probably come in handy when we start working with the δ -function.
- We can prove these five equalities with the notion of equality defined above.
- Example: Proving equality 1.

Proof. Let $D_1(x) = x\delta(x)$ and $D_2(x) = 0$. Then

$$\int_{-\infty}^{\infty} dx \delta(x) x f(x) = x f(x) \Big|_{x=0} = 0$$

and

$$\int_{-\infty}^{\infty} dx 0 f(x) = 0$$

It follows by transitivity that the two integrals equal each other, so we must have $x\delta(x) = 0$ as desired. \square

- Equality 4 is the hardest to prove. We will have a constant $D_1(x)$ equal to

$$D_1(x) = \int_{-\infty}^{\infty} dy \delta(a-y)\delta(y-b)$$

- Fourier transforms (FT) of δ -functions.
- Recall:

- The FT of the function $\phi(x)$ is

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

- The inverse FT is

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

- We call the FT of $\delta(x - x_0)$ the function

$$\tilde{\phi}(k; x_0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx e^{-ikx} \delta(x - x_0) = \frac{1}{\sqrt{2\pi}} e^{-ikx} \Big|_{x=x_0} = \frac{1}{\sqrt{2\pi}} e^{-ikx_0}$$

- In addition:

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{ikx} \qquad \tilde{\delta}(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dx e^{-ikx}$$

- Matt explains the FT in terms of decomposing sums of sines and cosines.
- Now the physics starts!
- Expectation values.
- So far, we have the wavefunction $\psi(x)$, which mysteriously contains information on the particle.
 - It solves the Schrödinger equation.
- $|\psi(x)|^2$ gives the probability density of finding the particle at x .
- The expectation value of some function $f(x)$ is

$$\langle f(x) \rangle = \int_{-\infty}^{\infty} dx \psi^*(x) f(x) \psi(x)$$

- 1D momentum \hat{p} can be written as the operator $-i\hbar \partial/\partial x$. Thus,

$$\langle p \rangle = \int_{-\infty}^{\infty} dx \psi^* = \int_{-\infty}^{\infty} dx \psi^* \left(-i\hbar \frac{\partial \psi}{\partial x} \right)$$

- This holds for n^{th} powers:

$$\langle \hat{p}^n \rangle = \int_{-\infty}^{\infty} dx \psi^* (-i\hbar)^n \frac{\partial^n \psi}{\partial x^n}$$

- Example (PSet 1, Q2): Prove that

$$\langle f(p) \rangle = \int_{-\infty}^{\infty} dk f(\hbar k) |\tilde{\psi}(k)|^2$$

Proof. Start from

$$\langle f(p) \rangle = \int_{-\infty}^{\infty} dx \psi^*(x) f(p) \psi(x)$$

Taylor expand about $f(0)$:

$$\begin{aligned}
 f(p) &= f(0) + \left. \frac{\partial f}{\partial p} \right|_{p=0} p + \frac{1}{2!} \left. \frac{\partial^2 f}{\partial p^2} \right|_{p=0} p^2 + \cdots = \sum_{n=0}^{\infty} \frac{1}{n!} \left. \frac{\partial^n f}{\partial p^n} \right|_{p=0} p^n \\
 &= \int_{-\infty}^{\infty} dx \psi^*(x) \sum_{n=0}^{\infty} \frac{1}{n!} \left. \frac{\partial^n f}{\partial p^n} \right|_{p=0} p^n \psi(x) \\
 &= \sum_{n=0}^{\infty} \frac{1}{n!} \left. \frac{\partial^n f}{\partial p^n} \right|_{p=0} \int_{-\infty}^{\infty} dx \psi^*(x) p^n \psi(x) \\
 &= \sum_{n=0}^{\infty} \frac{1}{n!} \left. \frac{\partial^n f}{\partial p^n} \right|_{p=0} \langle p^n \rangle
 \end{aligned}$$

This holds when

$$\begin{aligned}
 \langle p^n \rangle &= \int_{-\infty}^{\infty} dx \psi^*(x) (-i\hbar)^n \frac{\partial^n \psi}{\partial x^n} \\
 &= \int_{-\infty}^{\infty} dx \left(\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk e^{ikx} \psi(x) \right)^* (-i\hbar)^n \frac{\partial^n}{\partial x^n} \left(\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\ell e^{i\ell x} \tilde{\psi}(\ell) \right) \\
 &= \frac{(-i\hbar)^n}{2\pi} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} d\ell e^{-ikx} \tilde{\psi}^*(k) \tilde{\psi}(\ell) \frac{\partial^n}{\partial x^n} (e^{i\ell x}) \\
 &= \frac{(-i\hbar)^n}{2\pi} \int_{-\infty}^{\infty} dx dk d\ell e^{-ikx} \tilde{\psi}^*(k) \tilde{\psi}(\ell) (i\ell)^n e^{i\ell x} \\
 &= \int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} d\ell \tilde{\psi}^*(k) \tilde{\psi}(\ell) (\ell\hbar)^n \underbrace{\frac{1}{2\pi} \int_{-\infty}^{\infty} dx e^{i(\ell-k)x}}_{\delta(\ell-k)} \\
 &= \int_{-\infty}^{\infty} dk \tilde{\psi}^*(k) \tilde{\psi}(\ell) (\ell\hbar)^n \Big|_{\ell=k} \\
 &= \int_{-\infty}^{\infty} dk \tilde{\psi}^*(k) \tilde{\psi}(k) (k\hbar)^n \\
 &= \sum_{n=0}^{\infty} \frac{1}{n!} \left. \frac{\partial^n f}{\partial p^n} \right|_{p=0} \int_{-\infty}^{\infty} dk (k\hbar)^n |\tilde{\psi}(k)|^2 \\
 &= \int_{-\infty}^{\infty} dk |\tilde{\psi}(k)|^2 \underbrace{\sum_{n=0}^{\infty} \frac{1}{n!} \left. \frac{\partial^n f}{\partial p^n} \right|_{p=0} (k\hbar)^n}_{f(k\hbar)} \\
 &= \int_{-\infty}^{\infty} dk |\tilde{\psi}(k)|^2 f(k\hbar)
 \end{aligned}$$

□

- This example is much more complicated than the PSet. If we can understand 50% of it, we'll be great. If we didn't understand any of it, no worries.
- It sounds like we're not required to come to discussion session this quarter either.

2.5 Simple Cases of Time-Independent Potentials

1/12:

- Super snowy day, his wife told him only 5 students will show up, he takes a pic of the filled lecture hall with a kid at the front holding up a sign that says "We are more than 5," lol!!

- Review of equations.

- The operators $\hat{H}, \hat{p}, \hat{r}, \hat{V}$.
- The commutator $[p_i, r_j] = -i\hbar\delta_{ij}$.
- The relation between $\langle \hat{r} \rangle$ and $\langle \hat{p} \rangle$, and Ehrenfest's theorem.
- The Schrödinger equation.
- The following equality from last time

$$\langle \psi | \hat{O} \psi \rangle = \langle \hat{O}^\dagger \psi | \psi \rangle = \langle \psi | \hat{O} | \psi \rangle = \int d^3\vec{r} \psi^* \hat{O} \psi$$

- A Hermitian operator is one for which $\hat{O}^\dagger = \hat{O}$.
- These have real mean values and observables.

- **Incompatible** (operators): Two operators \hat{O}_1, \hat{O}_2 for which the following condition is met. *Constraint*

$$[\hat{O}_1, \hat{O}_2] \neq 0$$

- Means that you can't simultaneously determine the values of the observables associated with \hat{O}_1, \hat{O}_2 with infinite precision.
- Mathematically, this means that

$$\sigma_{\hat{O}_1} \sigma_{\hat{O}_2} \geq \frac{1}{2} \left| \langle \psi | [\hat{O}_1, \hat{O}_2] | \psi \rangle \right|$$

- We now start discussing time-independent potentials.
- What is important about these in classical mechanics?
 - Energy is conserved.
 - Classically, we demonstrated this by taking the equation

$$\begin{aligned} \vec{v} \cdot \frac{d}{dt} \left(m \frac{d\vec{r}}{dt} \right) &= -\vec{\nabla} V(\vec{r}) \cdot \frac{d\vec{r}}{dt} \\ \frac{d}{dt} \left(\frac{m\vec{v}^2}{2} \right) &= -\frac{d}{dt} (V(\vec{r})) \\ \frac{d}{dt} \left(\frac{m\vec{v}^2}{2} + V(\vec{r}) \right) &= 0 \\ \frac{dE}{dt} &= 0 \end{aligned}$$

- The equivalent expression in quantum mechanics is that

$$\frac{d}{dt} \left(\langle \psi | \hat{H} | \psi \rangle \right) = 0$$

- We now prove this expression.
- Start by considering the time variation of a generic Hermitian operator \hat{O} , i.e., we want

$$\frac{d}{dt} \left(\int d^3\vec{r} \psi^* \hat{O} \psi \right) = \frac{d}{dt} \left(\langle \psi | \hat{O} | \psi \rangle \right)$$

- Essentially, we have

$$\begin{aligned}
 \frac{d}{dt} \left(\langle \psi | \hat{O} | \psi \rangle \right) &= \int d^3\vec{r} \frac{\partial \psi^*}{\partial t} \hat{O} \psi + \int d^3\vec{r} \psi^* \frac{\partial \hat{O}}{\partial t} \psi + \int d^3\vec{r} \psi^* \hat{O} \frac{\partial \psi}{\partial t} \\
 &= \int d^3\vec{r} \psi^* \hat{O} \frac{\partial \psi}{\partial t} + \langle \psi | \frac{\partial \hat{O}}{\partial t} | \psi \rangle + \int d^3\vec{r} \left(\hat{O} \frac{\partial \psi}{\partial t} \right)^* \psi \\
 &= \int d^3\vec{r} \left[\hat{O} \left(-\frac{i}{\hbar} \hat{H} \psi \right) \right]^* \psi + \int d^3\vec{r} \psi^* \left(-\frac{i}{\hbar} \hat{O} \hat{H} \psi \right) + \left\langle \psi \left| \frac{\partial \hat{O}}{\partial t} \right| \psi \right\rangle \\
 &= \frac{i}{\hbar} \int d^3\vec{r} \psi^* (\hat{H} \hat{O} - \hat{O} \hat{H}) \psi + \left\langle \psi \left| \frac{\partial \hat{O}}{\partial t} \right| \psi \right\rangle \\
 \frac{d}{dt} \left(\langle \psi | \hat{O} | \psi \rangle \right) &= \frac{i}{\hbar} \langle \psi | [\hat{H}, \hat{O}] | \psi \rangle + \left\langle \psi \left| \frac{\partial \hat{O}}{\partial t} \right| \psi \right\rangle
 \end{aligned}$$

- In the first step, we move the derivative into the integral and do a tripartite product rule.
- The last statement above is a general statement that applies to all Hermitian operators \hat{O} , that is, all observables.
- Now, we can simply plug in $\hat{O} = \hat{H}$. Since the commutator of the Hamiltonian with itself is zero and $\partial \hat{H} / \partial t = 0$ by hypothesis (for a time-independent potential), we have that $d/dt (\langle \psi | \hat{H} | \psi \rangle) = 0$, as desired.
- Wagner reproves that $[\hat{p}_x, \hat{x}] = -i\hbar$.
 - Analogously, he proves that $[\hat{p}_x, \hat{y}] = 0$.
 - Relevant to PSet 1, Q3b!
- Implication: You *can* have an operator with a perfectly defined x -momentum and y -position.
- Another new derivation:

$$\begin{aligned}
 [\hat{p}_x, \hat{V}(\vec{r})]f &= -i\hbar \frac{\partial}{\partial x} (V(\vec{r})f) + i\hbar V(\vec{r}) \frac{\partial f}{\partial x} \\
 &= -i\hbar \frac{\partial V}{\partial x} f
 \end{aligned}$$

- What if we want to figure out $[\hat{p}, \hat{V}(\vec{r})]$?
 - Start off with the expression we derived above.

$$\frac{\partial}{\partial t} \left(\langle \psi | \hat{p} | \psi \rangle \right) = \frac{i}{\hbar} \langle \psi | [\hat{H}, \hat{p}] | \psi \rangle = \frac{i}{\hbar} (i\hbar \langle \psi | \vec{\nabla} V | \psi \rangle) = - \langle \psi | \vec{\nabla} V | \psi \rangle$$

- Moving on, let's try solving the Schrödinger equation with a separable ansatz,

$$\psi(\vec{r}, t) = \psi(\vec{r})\phi(t)$$

- This works because the left side of the Schrödinger equation doesn't operate on the position, and the right side doesn't operate on the time.
- Let's begin.

$$\begin{aligned}
 -\frac{\hbar^2}{2m} \vec{\nabla}^2 \psi(\vec{r}, t) + V(\vec{r})\psi(\vec{r}, t) &= i\hbar \frac{\partial}{\partial t} (\psi(\vec{r}, t)) \\
 \phi(t) \left[-\frac{\hbar^2}{2m} \vec{\nabla}^2 \psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) \right] &= i\hbar \psi(\vec{r}) \frac{\partial}{\partial t} (\phi(t)) \\
 \frac{1}{\psi(\vec{r})} \left[-\frac{\hbar^2}{2m} \vec{\nabla}^2 \psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) \right] &= \frac{i\hbar}{\phi(t)} \frac{\partial}{\partial t} (\phi(t))
 \end{aligned}$$

- Now the two sides of the above equation are functions of different variables, so they cannot be equal *unless* they are equal to a constant, which we'll call E . This allows us to split the above equation into two:

$$\begin{aligned}\frac{1}{\psi(\vec{r})}\hat{H}\psi(\vec{r}) &= E & \frac{i\hbar}{\phi(t)}\frac{\partial}{\partial t}(\phi(t)) &= E \\ \hat{H}\psi(\vec{r}) &= E\psi(\vec{r}) & \phi(t) &= A\exp\left(-\frac{iEt}{\hbar}\right)\end{aligned}$$

■ A is a constant of integration.

- We also have that

$$E_n = \langle \psi_n | \hat{H} | \psi_n \rangle$$

■ This means that the eigenstates of \hat{H} correspond to eigenvalues E_n .

- Thus, we have

$$\psi_n(\vec{r}, t) = \psi_n(\vec{r}) \exp\left(-\frac{iE_n t}{\hbar}\right)$$

- Note that we assume that we have renormalized every ψ_n written this way from here on out, pulling A and anything with it into $\psi_n(\vec{r})$.

- When $m \neq n$, we can obtain an important rule:

$$\begin{aligned}\langle \psi_m | \hat{H} | \psi_n \rangle &= E_n \langle \psi_m | \psi_n \rangle = E_m \langle \psi_m | \psi_n \rangle \\ (E_n - E_m) \langle \psi_m | \psi_n \rangle &= 0\end{aligned}$$

- It follows that if $E_m \neq E_n$, then $\langle \psi_m | \psi_n \rangle = 0$!

- Now let

$$\psi = \sum_n c_n \psi_n(\vec{r}) \exp\left(-\frac{iE_n t}{\hbar}\right)$$

- Then

$$\begin{aligned}\langle \psi | \psi \rangle &= \sum_{m,n} c_m^* c_n \exp\left(-\frac{i}{\hbar}(E_m - E_n)t\right) \langle \psi_m | \psi_n \rangle \\ &= \sum_m |c_m|^2\end{aligned}$$

- This follows from the fact that $\langle \psi_m | \psi_n \rangle = 1$.

- Last note.

$$\begin{aligned}\langle \psi | \hat{H} | \psi \rangle &= \sum_{m,n} c_m^* c_n \exp\left(-\frac{i}{\hbar}(E_m - E_n)t\right) \underbrace{\langle \psi'_m | \hat{H} | \psi_n \rangle}_{E_n \langle \psi_m | \psi_n \rangle} \\ &= \sum_m |c_m|^2 E_m\end{aligned}$$