

## 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,  $\psi$  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  $\psi$  is complex in general and thus has a nontrivial complex conjugate).

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

We will use the above two equations to substitute into the following algebraic derivation.

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

as desired. □

- How does everything cancel from the long line to the following line in the above proof??
- In quantum mechanics, we have **observables** which are in one-to-one correspondence with operators.

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

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.
- Once again,

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

Involves integration by parts?? Perhaps via

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

What is the takeaway??

- 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  $\psi$ , 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  $\langle\psi_i|\hat{O}|\psi_j\rangle := \int d^3\vec{r} \psi_i^* \hat{O} \psi_j$ .

- 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  $\psi_n$  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  $\psi_n$  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  $\psi$  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  $\psi_n$  is an eigenstate of  $\hat{A} \dots$

– 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 “ $\psi$  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

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

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)

- PSet1, 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  $\delta$ -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  $f$ .

- $\delta$ -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  $\delta$ -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

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

and

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

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  $\delta$ -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  $n^{\text{th}}$  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

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

□

- 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.

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

- 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  $\psi_n$  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.

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