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.
  - $\hat{\vec{p}}$ is the momentum operator, defined as the differential operator $-i\hbar\vec{\nabla}$.
  - Expressing the Schrödinger equation in terms of $\hat{\vec{p}}$, 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.
  - $\langle\hat{\vec{r}}\rangle$ is the mean position, and $\langle\hat{\vec{p}}\rangle$ is the mean momentum.
    - The mean position and mean momentum satisfy the classical relation, i.e., $\mathrm{d}\langle\hat{\vec{r}}\rangle/\mathrm{d}t = \langle\hat{\vec{p}}\rangle/m$.
- **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.

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

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

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

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

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

This means that altogether,

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

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

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

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
$$\hat{O}_{ij} := \int \mathrm{d}^3\vec{r}\ \psi_i^*\hat{O}\psi_j$$
  - 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
$$\int \mathrm{d}^3\vec{r}\ \psi^*\hat{O}\psi = \sum_{i,j}\int \mathrm{d}^3\vec{r}\ c_i^*\psi_i^*\hat{O}c_j\psi_j = \sum_{i,j} c_i^*c_j\hat{O}_{ij}$$
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:
$$\int \mathrm{d}^3\vec{r}\ \psi_i^*(-i\hbar\vec{\nabla}\psi_j) = \left(\int \mathrm{d}^3\vec{r}\ \psi_j^*(-i\hbar\vec{\nabla}\psi_i)\right)^* = \int \mathrm{d}^3\vec{r}\ \psi_j(i\hbar\vec{\nabla}\psi_i^*) \to -\int \mathrm{d}^3\vec{r}\ \vec{\nabla}\psi_j(i\hbar\psi_i^*)$$
  - To prove the leftmost equality above, we can use integration by parts as follows.
$$\begin{aligned}\int \mathrm{d}^3\vec{r}\ \psi_j(i\hbar\vec{\nabla}\psi_i^*) &= i\hbar\int \mathrm{d}^3\vec{r}\ \vec{\nabla}(\psi_j\psi_i^*) - \int \mathrm{d}^3\vec{r}\ \vec{\nabla}\psi_j(i\hbar\psi_i^*)\\ &= i\hbar\vec{\nabla}\int \mathrm{d}^3\vec{r}\ (\psi_j\psi_i^*) - \int \mathrm{d}^3\vec{r}\ \vec{\nabla}\psi_j(i\hbar\psi_i^*)\\ &= i\hbar\vec{\nabla}0 - \int \mathrm{d}^3\vec{r}\ \vec{\nabla}\psi_j(i\hbar\psi_i^*)\\ &= -\int \mathrm{d}^3\vec{r}\ \vec{\nabla}\psi_j(i\hbar\psi_i^*)\end{aligned}$$
    - 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 $\int \mathrm{d}^3\vec{r}\ \psi_m^*\psi_n = \delta_{mn}$.
  - 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
$$\int \mathrm{d}^3\vec{r}\ \psi_m^*\psi = \int \mathrm{d}^3\vec{r}\psi_m^*\sum_n c_n\psi_n = c_m$$
  - One more analogy: $\vec{x}^TA\vec{x} = A_{xx}$ 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: $\hat{\vec{p}}$, $\hat{H}$, $\hat{\vec{p}}^2/2m$, $V(\vec{r},t)$.
- **Adjoint** (of $\hat{O}$): The operator defined according to the following rule. *Denoted by* $\boldsymbol{\hat{O}^\dagger}$. *Constraint*

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

  - 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" $\langle\psi_i|\psi_j\rangle := \int \mathrm{d}^3\vec{r}\ \psi_i^*\psi_j$.
  - We also have $\langle\psi_i|\hat{O}|\psi_j\rangle := \int \mathrm{d}^3\vec{r}\ \psi_i^*\hat{O}\psi_j$.
  - 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:

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

- We also have that

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

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

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

  in the form

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

- In Dirac notation, the Hermitian condition becomes

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

- We also have that

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

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

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

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

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

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

is an imaginary number and

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

is a real number.

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

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

  - Thus,

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

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*
$$\left(\int \mathrm{d}^3\vec{r}\ |f|^2\right)\left(\int \mathrm{d}^3\vec{r}\ |g|^2\right) \geq \left|\int \mathrm{d}^3\vec{r}\ fg^*\right|^2$$
  - 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.
$$\langle\psi|\hat{A}|\psi'\rangle = \left\langle\psi\middle|\hat{A}\psi'\right\rangle = \left\langle\hat{A}\psi\middle|\psi'\right\rangle \qquad \langle\psi|\hat{A}^2|\psi'\rangle = \left\langle\hat{A}\psi\middle|\hat{A}\psi'\right\rangle$$
  - Consequently, we have that
$$\begin{aligned}
\sigma_A^2\cdot\sigma_B^2 &= \langle\psi|(\hat{A} - \langle\hat{A}\rangle)^2|\psi\rangle\cdot\langle\psi|(\hat{B} - \langle\hat{B}\rangle)^2|\psi\rangle \\
&= \left\langle(\hat{A} - \langle\hat{A}\rangle)\psi\middle|(\hat{A} - \langle\hat{A}\rangle)\psi\right\rangle\cdot\left\langle(\hat{B} - \langle\hat{B}\rangle)\psi\middle|(\hat{B} - \langle\hat{B}\rangle)\psi\right\rangle \\
&\geq \left|\left\langle(\hat{A} - \langle\hat{A}\rangle)\psi\middle|(\hat{B} - \langle\hat{B}\rangle)\psi\right\rangle\right|^2 \\
&= \left|\langle\psi|(\underbrace{\hat{A} - \langle\hat{A}\rangle}_{\Delta\hat{A}})(\underbrace{\hat{B} - \langle\hat{B}\rangle}_{\Delta\hat{B}})|\psi\rangle\right|^2
\end{aligned}$$

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*

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

- **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* $\delta(x - x_0)$. *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:

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

- Examples.

1. $$
\int_{-5}^{5} \mathrm{d}x\, \delta(x + 4)(x^2 - 3x + 4) = x^2 - 3x + 4\Big|_{x=-4} = 32
$$

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: $D_1(x) = \delta(x+3)\mathrm{e}^{-3x^2}$.
  - We say that $D_1(x) = D_2(x)$ if

    $$\int_{-\infty}^{\infty} \mathrm{d}x\, D_1(x)f(x) = \int_{-\infty}^{\infty} \mathrm{d}x\, D_2(x)f(x)$$

    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. $\int_{-\infty}^{\infty} \mathrm{d}x\, \delta(a-x)\delta(x-b) = \delta(a-b)$.
  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

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

and

$$\int_{-\infty}^{\infty} \mathrm{d}x\, 0f(x) = 0$$

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

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

- Fourier transforms (FT) of δ-functions.
- Recall:
  - The FT of the function $\phi(x)$ is

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

- The inverse FT is

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

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

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

- In addition:

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

- 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

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

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

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

  - This holds for n^{th} powers:

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

- Example (PSet 1, Q2): Prove that

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

Proof. Start from

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

Taylor expand about $f(0)$:

$$\begin{aligned}
f(p) = f(0) + \frac{\partial f}{\partial p}\bigg|_{p=0} p + \frac{1}{2!}\,\frac{\partial^2 f}{\partial p^2}\bigg|_{p=0} p^2 + \cdots &= \sum_{n=0}^{\infty}\frac{1}{n!}\,\frac{\partial^n f}{\partial p_n^n}\bigg|_{p=0}\\
&= \int_{-\infty}^{\infty} \mathrm{d}x\, \psi^*(x)\sum_{n=0}^{\infty}\frac{1}{n!}\,\frac{\partial^n f}{\partial p^n}\bigg|_{p=0} p^n\psi(x)\\
&= \sum_{n=0}^{\infty}\frac{1}{n!}\,\frac{\partial^n f}{\partial p^n}\bigg|_{p=0}\int_{-\infty}^{\infty} \mathrm{d}x\, \psi^*(x)p^n\psi(x)\\
&= \sum_{n=0}^{\infty}\frac{1}{n!}\,\frac{\partial^n f}{\partial p^n}\bigg|_{p=0}\langle p^n\rangle
\end{aligned}$$

This holds when

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

□

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

$$\left\langle\psi\middle|\hat{O}\psi\right\rangle = \left\langle\hat{O}^\dagger\psi\middle|\psi\right\rangle = \langle\psi|\hat{O}|\psi\rangle = \int \mathrm{d}^3\vec{r}\;\psi^*\hat{O}\psi$$

  - 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

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

- The equivalent expression in quantum mechanics is that

$$\frac{\mathrm{d}}{\mathrm{d}t}\Big(\langle\psi|\hat{H}|\psi\rangle \Big) = 0$$

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

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

  - Essentially, we have

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

    - 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 $\partial\hat{H}\big/\partial t = 0$ by hypothesis (for a time-independent potential), we have that $\mathrm{d}/\mathrm{d}t\left(\langle\psi|\hat{H}|\psi\rangle\right) = 0$, as desired.

- Wagner reproves that $[\hat{\vec{p}}_x, \hat{\vec{x}}] = -i\hbar$.
  - Analogously, he proves that $[\hat{\vec{p}}_x, \hat{\vec{y}}] = 0$.
  - Relevant to PSet 1, Q3b!
- Implication: You *can* have an operator with a perfectly defined x-momentum and y-position.
- Another new derivation:

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

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

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

- 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.

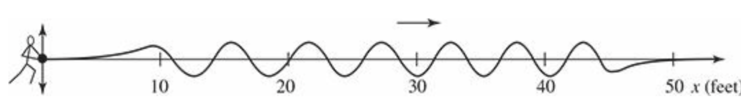
- Thus, we have
$$\psi_n(\vec{r},t)=\psi_n(\vec{r})\exp\left(-\frac{iE_nt}{\hbar}\right)$$
  - Note that we assume that we have renormalized every ψ_n written this way from here on out, absorbing A and anything with it into $\psi_n(\vec{r})$.
- When $m\neq n$, we can obtain an important rule:
$$\langle\psi_m|\hat{H}|\psi_n\rangle=E_n\langle\psi_m|\psi_n\rangle=E_m\langle\psi_m|\psi_n\rangle$$
$$(E_n-E_m)\langle\psi_m|\psi_n\rangle=0$$
  - It follows that if $E_m\neq E_n$, then $\langle\psi_m|\psi_n\rangle=0$!
- Now let
$$\psi=\sum_n c_n\psi_n(\vec{r})\exp\left(-\frac{iE_nt}{\hbar}\right)$$
  - 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.
$$\begin{aligned}\langle\psi|\hat{H}|\psi\rangle&=\sum_{m,n}c_m^*c_n\exp\left(-\frac{i}{\hbar}(E_m-E_n)t\right)\underbrace{\langle\psi_m'|\hat{H}|\psi_n\rangle}_{E_n\langle\psi_m|\psi_n\rangle}\\&=\sum_m|c_m|^2E_m\end{aligned}$$

2.6 Chapter 1: The Wave Function

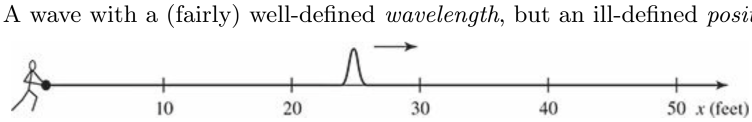
From Griffiths and Schroeter (2018).

Section 1.6: The Uncertainty Principle

1/29: - Qualitative justification of the uncertainty principle.



(a) A wave with a (fairly) well-defined *wavelength*, but an ill-defined *position*.



(b) A wave with a (fairly) well-defined *position*, but an ill-defined *wavelength*.

Figure 2.1: Visualizing the uncertainty principle.

  - Consider someone shaking a rope.

        - If they do so a lot, you get a wave with a well-defined wavelength and ill-defined position.
        - If they just shake it once, you get a wave with a well-defined position and ill-defined wavelength.
    - Thus, we see that there is a tradeoff between measuring the precision of wavelength and position.
    - This discussion is adapted from a quantitative theorem of Fourier analysis that is beyond the scope of the book.
- For a wave function, recall that de Brogelie said $\lambda \propto 1/p$, so the above relation between the uncertainties in position and wavelength becomes — for a quantum particle — a relation between the uncertainties in position and momentum.
- The Heisenberg Uncertainty Principle is stated, but not proven until Chapter 3.