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).

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

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

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

as desired. $\square$

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

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.
- Once again,

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

Involves integration by parts?? Perhaps via

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

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

- **Commutator** (of $\hat{O}_1, \hat{O}_2$): The operator defined as follows. *Denoted by* $[\hat{\boldsymbol{O}}_{\mathbf{1}}, \hat{\boldsymbol{O}}_{\mathbf{2}}]$. *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* $\{\hat{\boldsymbol{O}}_{\mathbf{1}}, \hat{\boldsymbol{O}}_{\mathbf{2}}\}$. *Given by*

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