

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).

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

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

- 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 $\hat{A} \dots$

– 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 “ 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)

- 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.