

# PHYS 23410 (Quantum Mechanics I) Notes

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# Week 1

## Origins of Quantum Mechanics

### 1.1 Historical Perspective

- 1/3:
- Intro to Wagner.
    - Will be teaching both Quantum I-II.
    - The structure of the course is explained in the syllabus on Canvas.
    - Every Friday, we get a new PSet due the next Friday.
      - This Friday, we will probably not get a PSet; PSet 1 will be handed out on Friday the 12th.
    - 50% of our grade is PSets; 50% is midterm and final.
      - This may fluctuate a bit.
    - Starting second week, we'll have 3 regular meetings each week.
    - If you have any problems, please get in touch with Wagner or the TAs!
    - Email: elcwagner@gmail.com.
    - OH will probably be on Wednesdays.
    - PSets posted on Canvas; solutions posted on Canvas after the deadline, too!
    - If there is something missing from Canvas, contact Wagner.
  - Announcement.
    - No discussion sections today most likely; write to the TAs to confirm or if we want to discuss anything with the TAs.
    - Wagner will *hopefully* (not certainly) be back on Fridays.
  - Outline of the course.
    1. Historical perspective.
      - Particle wave duality.
      - Uncertainty principle
    2. Schrödinger equation and the wave function.
    3. Formalism — observables in QM.
    4. Time-independent potentials.
      - One-dimensional problems.
    5. Angular momentum.
    6. Three dimensional problems.

- The hydrogen atom.
- 7. Spin, fermions, and bosons.
- 8. Symmetries and conservation laws.
- We now begin discussing the origins of quantum mechanics.
- **Photoelectric effect:** Electrons ejected from a metal when irradiated with light behave in a strange way.
  - In 1887, Hertz discovered this effect.
  - By 1905, it was clear that...
    1. No electrons were emitted unless the frequency of light was above a threshold value;
    2. The kinetic energy of the electrons grew linearly with frequency;
    3. The number of electrons depended on the light intensity.
  - These were three very strange phenomena.
  - In 1905, Einstein proposed a radical solution to this problem:
    1. Light is composed of **quanta**, that today we call **photons**.
    2. Each photon's energy is proportional to the frequency of light.
  - Essentially, Einstein said that if we model light this way, our model works.
  - Thus, the kinetic energy of the electrons is given by

$$K = h\nu - W$$

where  $h\nu$  is the kinetic energy of the photon and  $W$  is the minimum energy necessary to separate the electrons from the metal.

- Assuming the intensity to be proportional to the number of photons, we obtain the right behavior.
- The constant that relates the energy of the photon to its frequency is

$$h = 6.626 \times 10^{-34} \text{ J s} = 4.125 \times 10^{-15} \text{ eV s}$$

and had been introduced before by Planck in 1900 to solve the so-called black body radiation problem.

- Planck, however, thought of light emitted in quanta as a description of the emission process and not as the nature of light. In Planck's derivation, the average energy of the radiation emitted at a given frequency and temperature was given by a simple average weighted by Boltzmann factors:

$$\langle E \rangle = \frac{\sum n h \nu e^{-h n \nu / k T}}{\sum e^{-h n \nu / k T}} = \frac{h \nu}{e^{h \nu / k T} - 1}$$

- $h \nu$  is photon energy, and the  $e$  term is a Boltzmann factor.
- Boltzmann factors won't play a further role in this course (phew!).
- This implied a suppression for large frequencies instead of the classical value of  $kT$ . This value had been obtained for  $h \rightarrow 0$ , and it implied an unobserved infinite emission energy when summed over all frequencies!
- We now look into some implications of light quanta. Specifically, we will look at...
  - **Compton scattering;**
  - Light spectra;
  - Wave aspect of particles.

- **Compton scattering:**<sup>[1]</sup> The inelastic scattering of light off of a charged particle, resulting in a decrease in energy of the photon.

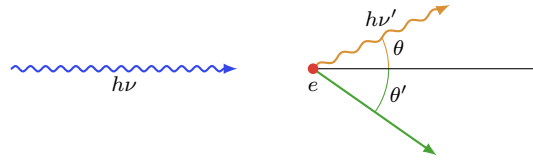


Figure 1.1: Compton scattering.

- Further confirmation of the existence of quanta of light came from the study of its scattering with electrons.
- Two properties were observed:
  1. Outgoing light had a different frequency than incoming.
  2. Frequency of the outgoing light depended on the emission angle.
- Let's treat photons as relativistic particles. Conservation of energy and momentum should be imposed. Then we have...
  1.  $h\nu + m_e c^2 = h\nu' + E_e$  — Energy.
  2.  $h\nu = h\nu' \cos \theta + c|p_e| \cos \theta'$  — Momentum.
  3.  $h\nu' \sin \theta = c|p_e| \sin \theta'$  — Momentum.
- Where do these equations come from?
  - Fact:  $|p| = E/c$ .
  - Equations 2,3 have been multiplied through by  $c$ !
- But we know that  $E_e^2 = m_e^2 c^4 + c^2 |p_e|^2$ .
  - “This should have been taught in a previous course.” It wasn't for me. What else did I miss, and where can I read about it??
- Hence, from (1),

$$(h\nu - h\nu' + m_e c^2)^2 = m_e^2 c^4 + c^2 |p_e|^2$$

- In addition,  $(2)^2 + (3)^2$  yields

$$c^2 |p_e|^2 = (h\nu - h\nu' \cos \theta)^2 + (h\nu' \sin \theta)^2$$

- By substituting the second expression into the first, expanding, cancelling the common  $m_e^2 c^4$ ,  $(h\nu)^2$  and  $(h\nu')^2$  factors on left and right, and algebraically rearranging, we get

$$2m_e c^2 (h\nu - h\nu') = 2h^2 \nu \nu' (1 - \cos \theta)$$

$$\frac{1}{\nu'} - \frac{1}{\nu} = \frac{h}{m_e c^2} (1 - \cos \theta)$$

- This last result above is important!
- Observe that we get  $\nu = \nu'$  for  $h = 0$ ; this is the classical result!
- An alternate form of the above result may be obtained via the relation  $c = \lambda \nu$ :

$$\Delta \lambda = \lambda' - \lambda = \frac{h}{m_e c} (1 - \cos \theta)$$

- The quantity  $h/m_e c$  is called the **Compton wavelength** and plays an important role in atomic physics.

<sup>1</sup>Recall the brief allusion to this in CHEM30200Notes.

- Compton scattering experimental results are in full agreement with the light quanta predictions, i.e., the derivation just described!

- **Compton wavelength:** The quantity defined as follows. *Denoted by  $\lambda_c$ . Given by*

$$\lambda_c = \frac{h}{m_e c} = 2.426 \times 10^{-12} \text{ m}$$

- Light spectra.

- From the definition of the Compton wavelength, we have that the energy of an electron is

$$E_e = m_e c^2 = \frac{ch}{\lambda_c} = 511 \text{ keV}$$

- Since gamma rays are those with  $h\nu > 100 \text{ keV}$ ,  $\lambda_c$  corresponds to one of these.
- For comparison, visible light has a frequency of around  $10^{15} \text{ Hz}$ , implying that  $h\nu = 3 - 6 \text{ eV}$

- Wave aspect of particles.

- De Broglie, in 1923, speculated that since light behaved in a dual way (i.e., as a wave and also as a particle), so should any other particle in nature.
- For instance, electrons must have a wave-light behavior.
- Only difference between electrons and light is that electrons are massive (have mass), while light has a vanishing mass.
- Light has energy  $E = c|\vec{p}| = h\nu$  and momentum  $\vec{p} = (h/2\pi) \cdot \vec{k}$ , where  $\vec{k}$  is the **wavevector** having magnitude  $|\vec{k}| = 2\pi/\lambda$ .
- For massive particles,

$$E = \sqrt{c^2 \vec{p}^2 + m^2 c^4} = mc^2 \sqrt{1 + \frac{\vec{p}^2}{m^2 c^2}}$$

- For nonrelativistic particles,  $|\vec{p}| \ll mc$ , so we may expand the square root's Taylor expansion to first order to get

$$E = mc^2 + \frac{\vec{p}^2}{2m}$$

- Recall also that

$$\vec{p} = \hbar \vec{k}$$

- Scalar-wise, note that  $p = E/c = h\nu/c = h/\lambda = (h/2\pi)(2\pi/\lambda) = \hbar k$ .
- The derivation of angular momentum in the Bohr model yields the correct result (this one), even though the conceptual wave function used in the derivation is wrong.
- Review these derivations and the relation to here!

- It follows that

$$E - mc^2 = \frac{\vec{p}^2}{2m}$$

where  $E - mc^2$  is the kinetic energy

$$E_k = \hbar \omega$$

- These assumptions lead to the form of the wave equation.

- **Wavevector:** The vector with magnitude equal to the wavenumber  $2\pi/\lambda$  and direction perpendicular to the wavefront, that is, in the direction of wave propagation.

- Wagner believes that this was covered in PHYS 13300; it wasn't.



- **Reduced Planck constant:** Planck's constant divided by  $2\pi$ . Denoted by  $\hbar$ . Given by

$$\hbar = \frac{h}{2\pi}$$

- We now look into some implications of electrons being waves.
- The wave function for a free electron of momentum  $\vec{p}$  will be

$$\psi_e \sim e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

where  $\omega = 2\pi\nu$ .

- But if electrons are waves, then they can be represented in states that include the superposition of many wave functions.
- Take two such waves  $\psi_1(\vec{r}, t)$  and  $\psi_2(\vec{r}, t)$ .
- Then

$$\psi = \alpha_1 e^{i(\vec{k}_1 \vec{r} - \omega_1 t)} + \alpha_2 e^{i(\vec{k}_2 \vec{r} - \omega_2 t)}$$

is an acceptable electron wave function.

- If we interpret  $\hbar\vec{k}_1$  and  $\hbar\vec{k}_2$  as momentum, we see an important difference between classical and quantum mechanics: The electrons may be *simultaneously in two different momentum states*.
- Implication: There is in general no real “path” of the electron with a well-defined position and momentum. At most, one can define a “wave packet,” with a certain mean value of position and momentum.
- How do we justify that electrons also behave like waves? With a double slit experiment, of course!
- Double slit experiment.



Figure 1.2: Double slit experiment.

- Let's take a beam of electrons impacting a wall with two slits.
  - Note that the focusing sheet with the single slit is not shown in Figure 1.2.
- The electrons going through the slits are measured on a screen.
- Classically, one expects the total number of electrons to be the simple sum of those going through slits  $S1$  and  $S2$ .
  - If we cover one slit, we'll see one hump; if we cover the other slit, we'll see the other hump.
  - If both are uncovered, the humps will add to a big hump.
  - This is what's happening in Figure 1.2a.
- If electrons behave as waves, however, the wave function  $\psi = \psi_{S1} + \psi_{S2}$  will be the superpositions of the waves coming from  $S1$  and  $S2$ .
  - $|\psi|^2 = I$  — next class, we will justify this, but for now we just accept it.
- The intensity, proportional to the number of electrons, will be given by

$$|\psi|^2 = |\psi_{S1} + \psi_{S2}|^2 = |\psi_{S1}|^2 + |\psi_{S2}|^2 + (\psi_{S1}^* \psi_{S2} + \psi_{S2}^* \psi_{S1})$$

- Calling  $I_i := |\psi_{Si}|^2$ , the above equation transforms into

$$|\psi|^2 = I_1 + I_2 + 2\sqrt{I_1 I_2} \cos \delta$$

where  $\delta$  is the phase difference that will depend on the waves' wavelength and the difference of the distances of the screens to the slits.

- We will therefore see an interference pattern.
- The observations are in full agreement with this prediction.
- What is this mysterious  $\psi$ ?
  - We know that  $|\psi|^2$  is the density of probability of finding an electron in a given point.
  - Essentially, if you take a small volume  $\Delta V = \Delta x \Delta y \Delta z$ , then  $|\psi|^2 \Delta V$  is the probability of finding the electron in  $\Delta V$ .
  - Therefore, since the sum of all probabilities should be normalized to 1, we know that

$$\int_{-\infty}^{\infty} |\psi|^2 dx dy dz = 1$$

- Typical lectures will be 100% blackboard-based, not this format.
- He will deliver notes at least one day before each lecture.
- Tell him if the lecture pace isn't good.
- Do the lectures align with the textbooks at all?
  - Griffiths and Schroeter (2018) starts with the Schrödinger equation without motivation; Wagner doesn't like that, so he motivates it a bit and then goes with Griffiths and Schroeter (2018) from there.
  - Some historical perspective is good.
    - UChicago used to have a course called Modern Physics that covered physics that was no longer modern to do all this stuff, but then they concluded it was useless and this content can be summarized in one lecture (today's!).
    - Nowadays, the optional QM III covers advanced topics.
  - Most books (with rare exceptions) cover the same topics, so I can pretty much pick up any book I want to follow along with.
    - That being said, Landau and Lifshitz (1977) is far more advanced and not at all suitable for a first brush with the material, but it is beautiful and Wagner highly recommends it. Landau and Lifshitz (1977) provides great intuition.

## 1.2 The Wave Function and the Schrödinger Equation

1/5:

- Announcements.
  - Largely reiterates from last time.
  - 50-60% of the grade is related to PSet solutions.
- Last time:
  - We talked about both light *and* particles as waves.
  - We defined  $\vec{p} = \hbar \vec{k}$  and  $E = \vec{p}^2 / 2m = \hbar \omega$ .

- The general form for a free wave is

$$\psi = A \exp \left[ i(\vec{k} \cdot \vec{r} - \omega t) \right] = A \exp \left[ \frac{i}{\hbar} (\vec{p} \cdot \vec{r} - Et) \right]$$

- If we evaluate  $-i\hbar \vec{\nabla} \psi$  with  $\psi$  defined as above, then we get

$$-i\hbar \vec{\nabla} \psi = \vec{p} \psi$$

- In this course, we will denote differential operators with hats, e.g., the momentum operator is

$$\hat{p} = -i\hbar \vec{\nabla}$$

- Observe that if we apply the momentum operator twice, we obtain

$$(-i\hbar \vec{\nabla}) \cdot (-i\hbar \vec{\nabla}) = -\hbar^2 \vec{\nabla}^2$$

- Recall that the gradient operator is defined via

$$\vec{\nabla} := \vec{x} \frac{\partial}{\partial x} + \vec{y} \frac{\partial}{\partial y} + \vec{z} \frac{\partial}{\partial z}$$

where  $\vec{x}^2 = \vec{y}^2 = \vec{z}^2 = 1$ .

- Hence, by the definition of the dot product,

$$\vec{\nabla}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

- Observe that if we evaluate  $i\hbar \, d\psi/dt$  with  $\psi$  defined as above, then we get

$$i\hbar \frac{d\psi}{dt} = E\psi$$

- **Hamiltonian operator** (for a free particle): The operator defined as follows. *Denoted by  $\hat{H}$ . Given by*

$$\hat{H} = \frac{\hat{p}^2}{2m}$$

- Thus,

$$\hat{H}\psi = \frac{\vec{p}^2}{2m} \psi = \frac{p^2}{2m} \psi = E\psi = i\hbar \frac{\partial \psi}{\partial t}$$

which implies by transitivity that for a free particle,

$$\frac{\vec{p}^2}{2m} \psi = E\psi$$

- Recall that normally,

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

- Schrödinger postulated the **Schrödinger equation**.

- **Schrödinger equation**: The equation defined as follows. *Given by*

$$\begin{aligned} \hat{H}\psi &= i\hbar \frac{\partial}{\partial t} \psi \\ -\frac{\hbar^2}{2m} \vec{\nabla}^2 \psi + V(\vec{r}, t) \psi &= i\hbar \frac{\partial}{\partial t} \psi \end{aligned}$$

- What do we know about  $\psi$ ?

- Recall from last time that

$$\int_V |\psi|^2 d^3\vec{r}$$

represents the probability of finding the particle in the volume  $V$ .

- In particular, this means that we must have

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx dy dz |\psi|^2 = 1$$

- This greatly diverges from classical mechanics, where particles followed a well-defined path for which you could define a position and momentum at each point along the path.
- The Schrödinger equation has many nice properties. Examples:

1. Linearity part 1 (scalability): If  $\psi$  is a solution, then  $k\psi$  is a solution where  $k$  is a constant.

- This follows directly from the definition:

$$-\frac{\hbar^2}{2m} \vec{\nabla}^2(k\psi) + V(\vec{r}, t)k\psi = k \left[ -\frac{\hbar^2}{2m} \vec{\nabla}^2\psi + V(\vec{r}, t)\psi \right] = k \left[ i\hbar \frac{\partial}{\partial t} \psi \right] = i\hbar \frac{\partial}{\partial t} (k\psi)$$

2. Linearity part 2 (additivity): If  $\psi_1, \psi_2$  are solutions, then  $\psi_1 + \psi_2$  is a solution.

- This is — once again — because of the linearity of the differential operators involved:

$$\hat{H}(\psi_1 + \psi_2) = i\hbar \frac{\partial}{\partial t} (\psi_1 + \psi_2)$$

- Because of linearity, quantum mechanics is *easier* than classical mechanics in some sense.
- It follows from the two parts of linearity that if  $\psi_1, \dots, \psi_n$  are solutions and  $c_1, \dots, c_n$  are complex constants, then

$$\psi = \sum_{i=1}^n c_i \psi_i$$

is a solution.

- What if I want to find the mean value of the *position* of the particle defined by  $\psi$ ? Integrate over all space (I know that the particle will be somewhere there), and scale the probability of it being at each point by the distance to that point:

$$\langle \hat{\vec{r}} \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx dy dz |\psi(\vec{r}, t)|^2 \vec{r}$$

- Note that  $\hat{\vec{r}} = \vec{r}$ , i.e., the position operator is just the position!

- What if we want to find the mean value of the *momentum* of the particle defined by  $\psi$ ? We have to do something less obvious:

$$\langle \hat{\vec{p}} \rangle = \int d^3\vec{r} \psi^* (-i\hbar \vec{\nabla} \psi)$$

- Is there a rationale for this construction??

- Why is it the mean value of the operator, not the quantity?

- We will define the mean value of the quantity to be the mean value of the operator.

- Now let's relate mean momentum and position!

- Recall from classical mechanics that  $\vec{p} = m \, d\vec{r}/dt$ . Is there an analogy?
- Recall from E&M that  $\partial\rho/\partial t + \vec{\nabla} \cdot \vec{J} = 0$ ; this is a relationship between density and current density.
- The analogous equation in quantum mechanics is

$$\frac{\partial |\psi|^2}{\partial t} + \vec{\nabla} \left[ \frac{i\hbar}{2m} (\psi \vec{\nabla} \psi^* - \psi^* \vec{\nabla} \psi) \right] = 0$$

- In PSet 1, we will derive this equation from the Schrödinger equation by multiplying by  $\psi, \psi^*$  to the two sides and adding.
  - The derivation should be pretty straightforward.
- We now use this equation.
- Differentiate both sides of the  $\langle \hat{r} \rangle$  equation to get

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

- We now integrate by parts using

$$\int_{-\infty}^{\infty} dx \, f(x) \cdot \frac{d}{dx} g(x) = \int_{-\infty}^{\infty} dx \, \frac{d}{dx} [f(x) \cdot g(x)] - \int_{-\infty}^{\infty} dx \, g(x) \cdot \frac{d}{dx} f(x)$$

- In the three dimensional setting, we'll need the fact that

$$\frac{\partial}{\partial x_i} r_j = \delta_{ij}$$

where  $\delta$  denotes the Kronecker delta function.

- Thus, continuing from the above, we have that

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

- Ask about instances of notation changing.
- Note that in this course,  $\psi^*$  denotes the complex conjugate of  $\psi$ .
  - We don't use  $\bar{\psi}$  here because bars often indicate something else in physics.
- Last note: All observables are real in quantum mechanics!
  - This is because all operators associated with quantum mechanics are **Hermitian**.
- **Hermitian** (operator): An operator satisfying the following equation. *Constraint*

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

- As with matrices, we have some kind of equality with the complex conjugate.

## 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  $\langle \psi_i | \hat{O} | \psi_i \rangle = \hat{O}_{ii}$ .



# References

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