PHYS 23410 (Quantum Mechanics I) Notes

Steven Labalme

February 19, 2024

Weeks

List of Figures

List of Tables

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

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

  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:

$$\langle E\rangle = \frac{\sum nh\nu \mathrm{e}^{-h\nu/kT}}{\sum \mathrm{e}^{-h\nu/kT}} = \frac{h\nu}{\mathrm{e}^{h\nu/kT}-1}$$

    - $nh\nu$ 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 $h \to 0$, 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**:[1] The inelastic scattering of light off of a charged particle, resulting in a decrease in energy of the photon.

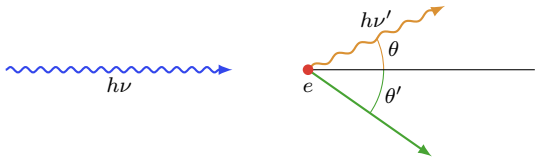


Figure 1.1: Compton scattering.

  - 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.

[1] 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* $\boldsymbol{\lambda_c}$. *Given by*

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

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

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

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

- 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,

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

  - 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 2π. *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

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

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

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

    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.

(a) Classical. (b) Wave-mechanical.

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 δ 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 ψ?
  - 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 ΔV.
  - Therefore, since the sum of all probabilities should be normalized to 1, we know that

$$\int_{-\infty}^{\infty} |\psi|^2 \,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z = 1$$

- 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

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

- If we evaluate $-i\hbar\vec{\nabla}\psi$ with ψ 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

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

- Observe that if we apply the momemtum 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 $i\hbar\,\mathrm{d}\psi/\mathrm{d}t$ with ψ defined as above, then we get

$$i\hbar\frac{\mathrm{d}\psi}{\mathrm{d}t} = E\psi$$

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

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

- 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,

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

- Schrödinger postulated the **Schrödinger equation**.
- **Schrödinger equation**: The equation defined as follows. *Also known as* **time-dependent Schrödinger equation**, **TDSE**. *Given by*

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

- What do we know about ψ?
  - Recall from last time that
$$\int_V |\psi|^2 \mathrm{d}^3\vec{r}$$
represents the probability of finding the particle in the volume V.
  - In particular, this means that we must have
$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\,|\psi|^2 = 1$$
- 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 ψ 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 ψ_1, ψ_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 $\psi_1, \ldots, \psi_n$ are solutions and $c_1, \ldots, c_n$ 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 ψ? 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:
$$\langle\hat{\vec{r}}\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\,|\psi(\vec{r},t)|^2\vec{r}$$
  - 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 ψ? We have to do something less obvious:
$$\langle\hat{\vec{p}}\rangle = \int \mathrm{d}^3\vec{r}\;\psi^*(-i\hbar\vec{\nabla}\psi)$$
  - 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 $\vec{p} = m\,\mathrm{d}\vec{r}/\mathrm{d}t$. 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 from the Schrödinger equation by multiplying by ψ, ψ^* to the two sides and adding.
  - The derivation should be pretty straightforward.
- We now use this equation.
- Differentiate both sides of the $\langle\hat{\vec{r}}\rangle$ equation to get

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

- We now integrate by parts using

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

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

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

  where δ denotes the Kronecker delta function.
- Thus, continuing from the above, we have that

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

- Ask about instances of notation changing.
- Note that in this course, ψ^* denotes the complex conjugate of ψ.
  - 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. *Also known as* **self-adjoint**. *Constraint*

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

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

1.3 G Chapter 0: Preface

From Griffiths and Schroeter (2018).

1/9:

- "Every competent physicist can 'do' quantum mechanics, but the stories we tell ourselves about what we are doing are as various" as can be (Griffiths & Schroeter, 2018, p. 11).
- "We do not believe one can intelligently discuss what quantum mechanics *means* until one has a firm sense of what quantum mechanics *does*," hence this book is devoted to teaching how to *do* quantum mechanics (Griffiths & Schroeter, 2018, p. 11).
- Mathematical prerequisites.
  - Legendre, Hermite, and Laguerre polynomials.
  - Spherical harmonics.
  - Bessel, Neumann, and Hankel functions.
  - Airy functions.
  - The Riemann zeta function.
  - Fourier transforms.
  - Hilbert spaces.
  - Hermitian operators.
  - Clebsch-Gordon coefficients.
- Griffiths and Schroeter (2018) recommend two math books for physicists that would explain the above concepts.

1.4 G Chapter 1: The Wave Function

From Griffiths and Schroeter (2018).

Section 1.1: The Schrödinger Equation

- All systems that occur at the microscopic level are conservative!
- The setup in classical mechanics: Use Newton's second law to find a given particle's trajectory $x(t)$ and then derive any other quantity (e.g., v, p, T) that you want from there.
- The setup in quantum mechanics: Use the Schrödinger equation to find a given particle's wave function $\psi(x,t)$.

Section 1.2: The Statistical Interpretation

- **Statistical interpretation**: $|\psi(x,t)|^2$ gives the probability of finding the particle at the point x at time t.
  - Attributed to Max Born.
- Probability as the area under a curve.
- **Quantum indeterminacy**: Even if you know everything the theory has to tell you about a given particle (e.g., the theory tells you its wave function), still you cannot predict with certainty the outcome of a simple experiment to measure the particle's position.
- Is quantum indeterminacy a fact of nature or a defect in the theory?
  - Big physical/philosophical question!

- Suppose you measure the position of a given particle, finding that its at point C.
  - Where was the particle just before measuring?
  - Three plausible answers: The **realist**, **orthodox**, and **agnostic** positions.
- **Realist** (position): The particle was at C.
  - "The position of the particle was never indeterminate, but was merely unknown to the experimenter" (Griffiths & Schroeter, 2018, p. 17).
  - If this is true, then quantum mechanics is an **incomplete** theory, i.e., we are missing some **hidden variable** needed to prove a complete description of the particle.
- **Orthodox** (position): The particle wasn't really anywhere. *Also known as* **Copenhagen interpretation**.
  - Implication: It was the act of measurement that forced the particle to "take a stand."
  - Implication: "Observations not only *disturb* what is to be measured, they *produce* it... we *compel* [the particle] to assume a definite position" (Griffiths & Schroeter, 2018, p. 17).
- **Agnostic** (position): Refuse to answer.
  - Only way to establish where the particle was before moving is to take two measurements, but we can't do this physically.
  - Thus, why even worry about the question!
- John Bell in 1964 showed that there is an observable corresponding to whether the particle has a precise position prior to measurement, eliminating agnosticism and making the distinction between realism and orthodoxy a (mostly) experimental question.
  - The orthodox position is the most likely current contender following the experiment.
- Measuring position twice consecutively must give the same value.
  - We account for this by saying that the wave function **collapses** to a spike at C that we can measure again quickly before the wave function spreads out anew.
- Double slit experiment with electrons.

Section 1.3: Probability

- Largely a review of MathChapter B from CHEM26100Notes. A few important, novel things are noted below.
- Why do we measure spread via squared terms?
  - The most obvious way to measure spread would be to find out how far each individual is from the average via $\Delta j = j - \langle j \rangle$ and then compute $\langle \Delta j \rangle$. But $\langle \Delta j \rangle = 0$ always.
  - What else could we do? We could take the absolute value of Δj. But this would be computationally complicated and involve lots of signs of which to keep track.
  - Thus, we get around both the zeroing out problem and the sign problem by squaring to get $\langle (\Delta j)^2 \rangle$.
- **Probability density**: The proportionality factor $\rho(x)$ such that $\rho(x)\,\mathrm{d}x$ is the probability that an individual lies between x and $x + \mathrm{d}x$.
- Example 1.2: A really interesting continuous probability problem! Come back to if I have time.

Section 1.4: Normalization

- Recall that a wave function ψ is not necessarily normalized right off the bat, but since we have scalar linearity, we can normalize it!
- This also means that we neglect any trivial solutions ($\psi = 0, \infty$) as not corresponding to real particles, since these wavefunctions can't be normalized.
- "Physically realizable states correspond to the **square-integrable** solutions to Schrödinger's equation" (Griffiths & Schroeter, 2018, p. 29).
- If we only normalized ψ at $t = 0$, how do we know that it will stay normalized as ψ evolves?
  - It is a property of the Schrödinger equation that ψ does stay normalized.
  - Without this fact, the whole statistical interpretation would break down.
- Griffiths and Schroeter (2018) essentially answer PSet 1, Q1.

Section 1.5: Momentum

- **Expectation value**: The average of measurements on an ensemble of identically prepared systems.
  - The expectation value is *not* the average of repeated measurements of the same particle (because measurement changes the particle).
- We now justify why expectation values are calculated the way they are.
  - To begin, we have as in class that

$$\begin{aligned}\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} &= \frac{\mathrm{d}}{\mathrm{d}t}\left(\int x|\psi|^2\,\mathrm{d}x\right)\\ &= \int x\frac{\partial}{\partial t}|\psi|^2\,\mathrm{d}x\\ &= \frac{i\hbar}{2m}\int x\frac{\partial}{\partial x}\left(\psi^*\frac{\partial\psi}{\partial x} - \frac{\partial\psi^*}{\partial x}\psi\right)\mathrm{d}x\end{aligned}$$

    We now invoke integration by parts. Let $u := x$ and $\mathrm{d}v := \partial/\partial x\,(\psi^*\,\partial\psi/\partial x - \partial\psi^*/\partial x\,\psi)\,\mathrm{d}x$. Then we obtain

$$= \frac{i\hbar}{2m}\left\{\left[x\left(\psi^*\frac{\partial\psi}{\partial x} - \frac{\partial\psi^*}{\partial x}\psi\right)\right]_{-\infty}^{\infty} - \int\left(\psi^*\frac{\partial\psi}{\partial x} - \frac{\partial\psi^*}{\partial x}\psi\right)\mathrm{d}x\right\}$$

    Since $\psi(\infty) = \psi^*(\infty) = \psi(-\infty) = \psi^*(-\infty) = 0$, the left term above goes to zero, leaving

$$\begin{aligned}&= -\frac{i\hbar}{2m}\int\left(\psi^*\frac{\partial\psi}{\partial x} - \frac{\partial\psi^*}{\partial x}\psi\right)\mathrm{d}x\\ &= -\frac{i\hbar}{2m}\left(\int\psi^*\frac{\partial\psi}{\partial x}\,\mathrm{d}x - \int\frac{\partial\psi^*}{\partial x}\psi\,\mathrm{d}x\right)\end{aligned}$$

    Now considering the right term above, let $u := \psi$ and $\mathrm{d}v := \partial\psi^*/\partial x\,\mathrm{d}x$. Then by both integration by parts and considering the behavior of ψ, ψ^* at $\pm\infty$ once again, we obtain

$$\begin{aligned}&= -\frac{i\hbar}{2m}\left[\int\psi^*\frac{\partial\psi}{\partial x}\,\mathrm{d}x - \left([\psi\psi^*]_{-\infty}^{\infty} - \int\psi^*\frac{\partial\psi}{\partial x}\,\mathrm{d}x\right)\right]\\ &= -\frac{i\hbar}{2m}\left[\int\psi^*\frac{\partial\psi}{\partial x}\,\mathrm{d}x - \left(0 - \int\psi^*\frac{\partial\psi}{\partial x}\,\mathrm{d}x\right)\right]\\ &= -\frac{i\hbar}{2m}\left(\int\psi^*\frac{\partial\psi}{\partial x}\,\mathrm{d}x + \int\psi^*\frac{\partial\psi}{\partial x}\,\mathrm{d}x\right)\\ &= -\frac{i\hbar}{m}\int\psi^*\frac{\partial\psi}{\partial x}\,\mathrm{d}x\end{aligned}$$

- All integrals above are over all space.
- We use $\partial/\partial x$ instead of $\vec{\nabla}$ because the book is only treating the one-dimensional case so far; the two operators are entirely analogous, though, by the definition of $\vec{\nabla}$!

– Aside: Interpreting the above result.

- It is unclear that we could even give a well-defined conceptualization of the velocity $\langle v \rangle$ of a quantum particle.
- It turns out that we can (see Chapter 3), but for now we will postulate that

$$\langle v \rangle := \frac{\mathrm{d}\langle x \rangle}{\mathrm{d}t}$$

– It is much more customary to work with the *momentum* $\langle p \rangle = m\langle v \rangle$ of a quantum particle.

– In terms of ψ, the above equation tells us that

$$\langle p \rangle = -i\hbar \int \psi^* \frac{\partial \psi}{\partial x} \, \mathrm{d}x$$

– Let's rewrite the above expressions for $\langle x \rangle, \langle p \rangle$ in a more suggestive way.

$$\langle x \rangle = \int \psi^* [x] \psi \, \mathrm{d}x \qquad\qquad \langle p \rangle = \int \psi^* [-i\hbar(\,\partial/\partial x\,)] \psi \, \mathrm{d}x$$

– Thus, we have derived expressions that we may call the **operators** representing position x and momentum p!

– Fact: "All classical dynamical variables can be expressed in terms of position and momentum" (Griffiths & Schroeter, 2018, p. 33).

- Example: $T = p^2/2m$.
- Example: $\vec{L} = \vec{r} \times \vec{p}$.

– Implication: To calculate the expectation value of any such quantity $Q(x, p)$, we simply replace every p by $-i\hbar(\,\partial/\partial x\,)$, insert the resulting operator between ψ^* and ψ, and integrate:

$$\langle Q(x,p) \rangle = \int \psi^* [Q(x, -i\hbar\,\partial/\partial x\,)] \psi \, \mathrm{d}x$$

- In Chapter 3, we will put the above equation on firmer theoretical footing.

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,

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

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

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: $\vec{x}^T A\vec{x} = A_{xx}$ 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: $\hat{\vec{p}}$, $\hat{H}$, $\hat{\vec{p}}^2/2m$, $V(\vec{r},t)$.
- **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 $\hat{A}\ldots$
  - 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.
$$\langle\psi|\hat{A}|\psi'\rangle = \left\langle\psi\middle|\hat{A}\psi'\right\rangle = \left\langle\hat{A}\psi\middle|\psi'\right\rangle \qquad\qquad \langle\psi|\hat{A}^2|\psi'\rangle = \left\langle\hat{A}\psi\middle|\hat{A}\psi'\right\rangle$$
  - 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,

$$= \Big| \langle\psi| \frac{1}{2}([\Delta\hat{A}, \Delta\hat{B}] + \{\Delta\hat{A}, \Delta\hat{B}\})|\psi\rangle \Big|^2$$
$$= \frac{1}{4}\Big| \langle\psi|[\Delta\hat{A}, \Delta\hat{B}] + \{\Delta\hat{A}, \Delta\hat{B}\}|\psi\rangle \Big|^2$$

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,

$$\geq \frac{1}{4}\Big| \langle\psi|[\hat{A}, \hat{B}]|\psi\rangle \Big|^2$$

- 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* $\boldsymbol{[\hat{O}_1, \hat{O}_2]}$. *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* $\boldsymbol{\{\hat{O}_1, \hat{O}_2\}}$. *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* $\boldsymbol{\delta(x - x_0)}$. *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. □

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

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

This holds when

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

□

- 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 $\mathrm{d}/\mathrm{d}t\,(\langle\psi|\hat{H}|\psi\rangle) = 0$, 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:

$$\frac{1}{\psi(\vec{r})}\hat{H}\psi(\vec{r}) = E \qquad\qquad \frac{i\hbar}{\phi(t)}\frac{\partial}{\partial t}(\phi(t)) = E$$

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r}) \qquad\qquad \phi(t) = A\exp\left(-\frac{iEt}{\hbar}\right)$$

    - 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.

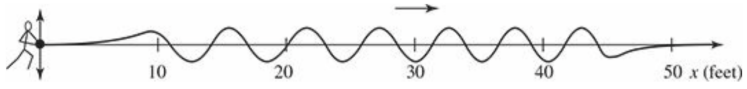
- Thus, we have
$$\psi_n(\vec{r},t) = \psi_n(\vec{r})\exp\left(-\frac{iE_nt}{\hbar}\right)$$
  - Note that we assume that we have renormalized every ψ_n written this way from here on out, absorbing A and anything with it into $\psi_n(\vec{r})$.
- When $m \neq n$, we can obtain an important rule:
$$\begin{aligned}\langle\psi_m|\hat{H}|\psi_n\rangle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

2.6 G Chapter 1: The Wave Function

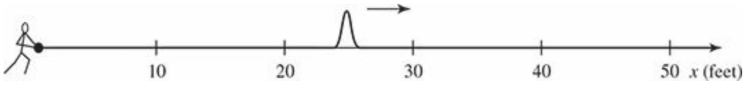
From Griffiths and Schroeter (2018).

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.

2.7 G Chapter 2: Time-Independent Schrödinger Equation

From Griffiths and Schroeter (2018).

Section 2.1: Stationary States

- Goes through solving the TDSE via separation of variables.
  - Remark: Separation of variables is "the physicist's first line of attack on any partial differential equation" (Griffiths & Schroeter, 2018, p. 43).
  - Griffiths and Schroeter (2018) finally addresses my criticism that separation of variables will restrict us to a tiny subset of solutions!
    - Answer: This is true, but it just so happens that the solutions we *do* get turn out to be of great interest. So essentially, this is "because it works" physics.

- **Time-independent Schrödinger equation**: The equation defined as follows. *Also known as* **TISE**. *Given by*
$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V\psi = E\psi$$

- The remaining sections of this chapter will focus on solving the TISE for various simple potentials.

- Three reasons why separable solutions are valuable.
  1. They are **stationary states**.
     - Every expectation value $\langle Q(x,p)\rangle$ is also constant in time.
     - In particular, $\langle\hat{\vec{x}}\rangle$ is constant so $\langle\hat{\vec{p}}\rangle = 0$.
  2. They are states of definite total energy.
     - Reproves that $\sigma_H^2 = 0$, and hence every measurement of the total energy is certain to return the value E.
  3. The general solution is a linear combination of separable solutions.
     - Essentially, we can prove that *every* solution to the TDSE can be written as
$$\psi(x,t) = \sum_{n=0}^{\infty} c_n\psi_n(x)\mathrm{e}^{-iE_nt/\hbar}$$

- **Stationary state**: A wave function $\psi(x,t)$ for which the probability density $|\psi(x,t)|^2$ does *not* depend on t.

- Example: The linear combination of two stationary states produces motion.

  - If $\psi(x,0) = c_1\psi_1(x) + c_2\psi_2(x)$, then we may compute that

$$|\psi(x,t)|^2 = c_1^2\psi_1^2 + c_2^2\psi_2^2 + 2c_1c_2\psi_1\psi_2\cos\left(\frac{E_2 - E_1}{\hbar}t\right)$$

- $|c_n|^2$ is the probability that a measurement of the energy would return the value E_n.
  - Proven in Chapter 3.
- It follows from this understanding that we must have Wagner's favorite two equations,

$$\sum_{n=0}^{\infty} |c_n|^2 = 1 \qquad\qquad \sum_{n=0}^{\infty} |c_n|^2 E_n = \langle \hat{H} \rangle$$

- Remark: "Because the constants $\{c_n\}$ are independent of time, so too is the probability of getting a particular energy, and, *a fortiori*, the expectation value of H. These are manifestations of energy conservation in quantum mechanics" (Griffiths & Schroeter, 2018, p. 47).

Week 3

Time-Independent Problems in 1D

3.1 Infinite Well Motion

1/17:

- We begin today by building up to the uncertainty principle another, more general way.
- Recall that what we are aiming for is

$$\Delta p_x \Delta x \geq \frac{\hbar}{2}$$

where $\Delta p_x, \Delta x$ are the uncertainties in the determination of the momentum and position, respectively:

$$(\Delta p_x)^2 = \langle (\hat{\vec{p}}_x - \langle \hat{\vec{p}}_x \rangle)^2 \rangle = \langle \hat{\vec{p}}_x{}^2 \rangle - \langle \hat{\vec{p}}_x \rangle^2 \qquad (\Delta x)^2 = \langle \hat{\vec{x}}^2 \rangle - \langle \hat{\vec{x}} \rangle^2$$

- Example of the uncertainty principle: For a plane wave, we know the momentum but not the position. That is, $\Delta x \to \infty$ and $\Delta p_x \to 0$.
- More generally, for a **wave packet**, we know only approximately the position and momentum.
- **Wave packet**: A continuous sum of waves of different frequencies. *Given by*

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) \mathrm{e}^{i(kx - \omega(k)t)} \, \mathrm{d}k$$

(a) A wave packet.

(b) Group and phase velocity.

Figure 3.1: Wave packets.

  - Note that the above formula only applies to the one dimensional case.
- Let's investigate the case of a wave packet of free particles.
  - In this case,

$$\omega(k) = \frac{\hbar k^2}{2m}$$

- This is derived from
$$\hbar\omega = E = \frac{p^2}{2m} = \frac{(\hbar k)^2}{2m}$$
by cancelling an $\hbar$ from both sides.

– Let's assume that $\phi(k)$ is a narrowly peaked function around a certain value k_0.

– Then we can expand
$$\begin{aligned}\omega(k) &= \omega(k_0) + \left.\frac{\mathrm{d}\omega}{\mathrm{d}k}\right|_{k=k_0}(k-k_0) + \cdots \\ &= \omega(k_0) + \left.\frac{\hbar k}{m}\right|_{k=k_0}(k-k_0) + \cdots \\ &= \omega(k_0) + \underbrace{\frac{\hbar k_0}{m}}_{\omega_0'}(k-k_0) + \cdots\end{aligned}$$

– Define $s := k - k_0$.

– Then $k = k_0 + s$ and $\mathrm{d}k = \mathrm{d}s$, so
$$\begin{aligned}\psi(x,t) &= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(k_0+s)\mathrm{e}^{i((k_0+s)x-(\omega(k_0)+\omega_0' s)t)}\,\mathrm{d}s \\ &= \frac{1}{\sqrt{2\pi}}\mathrm{e}^{i(k_0 x-\omega(k_0)t)}\int_{-\infty}^{\infty}\phi(k_0+s)\mathrm{e}^{is(x-\omega_0' t)}\,\mathrm{d}s\end{aligned}$$

– It follows that
$$|\psi(x,t)|^2 = \frac{1}{2\pi}\left|\int_{-\infty}^{\infty}\phi(k_0+s)\mathrm{e}^{is(x-\omega_0' t)}\,\mathrm{d}s\right|^2 = f(x-\omega_0' t)$$

- In words, the probability density is a function of $x - \omega_0' t$, so the packet moves with **group velocity** $\omega_0' = \hbar k_0/m = p_0/m$.

– Implication: The wave packet moves with a velocity that is equal ot the classical velocity
$$\left.\frac{\mathrm{d}\omega}{\mathrm{d}k}\right|_{k=k_0} = \frac{p_0}{m}$$

- **Group velocity**: A measure of the velocity of a wave packet. *Denoted by* $\boldsymbol{v_g}$, $\boldsymbol{v_{\mathrm{group}}}$. *Given by*
$$v_{\mathrm{group}} = \left.\frac{\mathrm{d}\omega}{\mathrm{d}k}\right|_{k=k_0}$$

- **Phase velocity**: A measure of the velocity of the ripples. *Denoted by* $\boldsymbol{v_p}$, $\boldsymbol{v_{\mathrm{phase}}}$. *Given by*
$$v_{\mathrm{phase}} = \frac{\omega(k_0)}{k_0} = \frac{\hbar k_0}{2m} = \frac{v_{\mathrm{group}}}{2}$$

- Explicit example of a wave packet: A **Gaussian wave packet**.

- **Gaussian wave packet**: A one-dimensional wave packet of the following form. *Given by*
$$\psi_0(x,t) = \left(\frac{2}{\pi\sigma^2}\right)^{1/4}\exp\left[-\frac{(x-v_g t)^2}{\sigma^2}\right]\mathrm{e}^{i(k_0 x - v_p t)}$$

– This means that we must have used the following definition of $\phi(k)$ in the original definition.
$$\phi(k) = \left(\frac{\sigma^2}{2\pi}\right)^{1/4}\exp\left[-\frac{\sigma^2(k-k_0)^2}{4}\right]$$

- Uncertainty analysis of a Gaussian wave packet.
  - The uncertainties Δx and Δk are associated with the widths of the Gaussians, as one can determine by computing. Indeed, at $t = 0$,

$$\langle \hat{\vec{x}} \rangle = 0 \qquad \langle \hat{\vec{x}}^{\,2} \rangle = (\Delta x)^2 \qquad \langle (k - k_0)^2 \rangle = (\Delta k)^2$$

    - Indeed, since $\langle k \rangle = k_0$, we know that $\langle (k - k_0)^2 \rangle = \langle k^2 \rangle - k_0^2$.
  - For Gaussians, normalized as $\int |\psi|^2 = 1$, we obtain

$$\left(\frac{1}{\pi\sigma^2}\right)^{1/2} \int_{-\infty}^{\infty} u^2 \exp\left(-\frac{u^2}{\sigma^2}\right) \mathrm{d}u = (\Delta u)^2 = \frac{\sigma^2}{2}$$

    - How do we get this??
  - It follows that the value of Δu coincides well with the departure from the central value for which the exponential in $|\psi|^2$ or $|\phi|^2$ is $\mathrm{e}^{-1/2}$.
  - Altogether, we get

$$\Delta x = \frac{\sigma}{2} \qquad \Delta k = \frac{1}{\sigma}$$

    so

$$\Delta x \Delta k = \frac{1}{2}$$
$$\Delta x \Delta p_x = \frac{\hbar}{2}$$

    for a Gaussian wave packet.
  - Implication: The Gaussian function minimizes the product of the position and momentum uncertainties!

- We now move onto discussing the **infinite square well** potential, a one-dimensional time-independent potential for which we can solve the Schrödinger equation exactly.

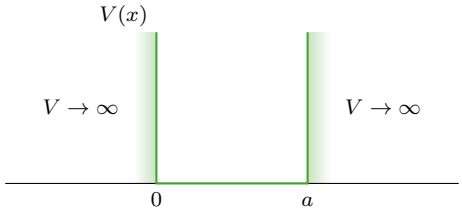


Figure 3.2: Infinite square well.

- **Infinite square well**: The potential energy function that vanishes for $0 < x < a$ and tends to infinity for $x \leq 0$ and $x \geq a$. *Given by*

$$V(x) = \begin{cases} 0 & 0 < x < a \\ \infty & \text{otherwise} \end{cases}$$

- We would like to obtain energy eigenstates for this potential. That is, we seek eigenvalues and eigenfunctions for

$$\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)\right]\psi(x) = E\psi(x)$$

  - Any such eigenstate ψ will have $\psi(x) = 0$ in the region of space where $V \to \infty$.

- Hence, the Schrödinger equation reduces to the boundary-value problem

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi \qquad\qquad \psi(0) = \psi(a) = 0$$

- The above ODE may be expressed in the following equivalent form

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\left(\frac{2mE}{\hbar^2}\right)\psi$$

- Observe that this ODE is of the same form as the classical harmonic oscillator equation $\mathrm{d}^2x/\mathrm{d}t^2 = -(k/m)x$. Thus, it admits a similar set of solutions:

$$\psi_n(x) = C\sin\left(\sqrt{\frac{2mE_n}{\hbar^2}}x\right) \qquad\qquad \sqrt{\frac{2mE_n}{\hbar^2}}a = n\pi,\ n = 1, 2, \ldots$$

- It follows that

$$E_n = \frac{\hbar^2 n^2\pi^2}{2ma^2}$$

- The coefficient C can be fixed via the normalization requirement, as follows.

$$\begin{aligned}
1 &= \int_0^a |\psi_n(x)|^2\,\mathrm{d}x \\
&= C^2\int_0^a \sin^2\left(\frac{\pi nx}{a}\right)\mathrm{d}x \\
&= C^2\int_0^a \frac{1-\cos\left(\frac{2\pi nx}{a}\right)}{2}\,\mathrm{d}x \\
&= \frac{C^2}{2}\left[\int_0^a \mathrm{d}x - \int_0^a \cos\left(\frac{2\pi nx}{a}\right)\mathrm{d}x\right] \\
&= \frac{C^2}{2}\Bigg[a - \underbrace{\frac{a}{2n\pi}\sin\left(\frac{2\pi nx}{a}\right)\Bigg|_0^a}_{0}\Bigg] \\
&= \frac{aC^2}{2} \\
C &= \sqrt{\frac{2}{a}}
\end{aligned}$$

- Therefore, the complete eigenfunctions and eigenvalues are

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{\pi nx}{a}\right) \qquad\qquad E_n = \frac{\hbar^2 n^2\pi^2}{2ma^2}$$

- A general solution is therefore given by the following, where ψ_n, E_n are defined as above.

$$\psi(x,t) = \sum_n c_n\psi_n(x)\mathrm{e}^{-iE_nt/\hbar}$$

- The probability density of the infinite square well potential is time-independent.

Proof. Observe that given any individual eigenstate of energy

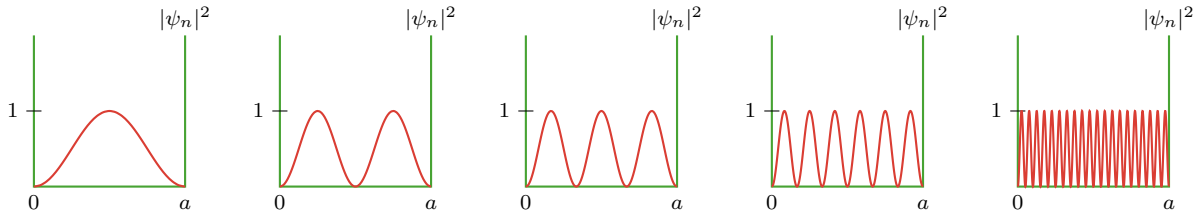
$$\psi_n(x,t) = \psi_n(x)\mathrm{e}^{-iE_nt/\hbar}$$

we have that

$$|\psi_n(x,t)|^2 = |\psi_n(x)|^2 = \frac{2}{a}\sin^2\left(\frac{\pi nx}{a}\right)$$

□

- Let's investigate the form of the probability density for a few n.



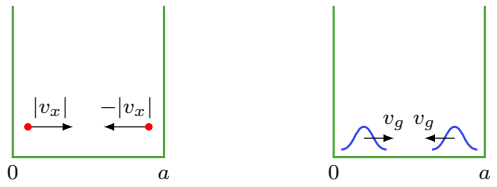
(a) $n = 1$. (b) $n = 2$. (c) $n = 3$. (d) $n = 6$. (e) $n \gg 1$.

Figure 3.3: Infinite square well probability density.

  - Recall that the average height of a sine wave is half its amplitude. Thus the average probability density is

$$\frac{1}{2} \cdot \frac{2}{a} = \frac{1}{a}$$

- Recovering "motion," in the sense that $\mathrm{d}/\mathrm{d}t\,(\langle\psi|\hat{\vec{x}}|\psi\rangle) \neq 0$



(a) Classical. (b) Quantum.

Figure 3.4: Infinite square well motion.

  - We obtain motion upon superimposing different eigenstate wave functions.
  - Guiding question: What would happen in the classical case of a particle in such a potential?
    - The particle would move first to the right with momentum $|p_x|$, then bounce against the wall at $x = a$ and change its momentum to $-|p_x|$, then bounce against the wall at $x = 0$ and change its momentum back to $|p_x|$, and so continue indefinitely.
  - In quantum mechanics, we can mimic the same behavior by forming a wave packet!
  - Since the particle moves free of forces between $0 < x < a$, one can try to build a Gaussian wave packet, similar to the one we discussed in the free particle case. The difference is that any wave function must vanish at $x = 0, a$, so it must be represented not by combinations of free waves e^{ikx} at $t = 0$ but by

$$\sin\left(\frac{\pi n x}{a}\right) = \frac{1}{2i}(\mathrm{e}^{i\pi n x/a} - \mathrm{e}^{-i\pi n x/a})$$

  - Define

$$k_n = \frac{\sqrt{2mE_n}}{\hbar} = \frac{\pi n}{a}$$

  - Now, what we want is a Gaussian with width Δx for $\Delta x \ll a$.
  - Recalling the free case $|\psi_0(x,t)|^2 = (1/\pi\sigma^2)^{1/2}\mathrm{e}^{-(x-v_g t)^2/2\sigma^2}$ with $\phi(k) = k\mathrm{e}^{-\sigma^2(k-k_0)^2}$, we would like to try

$$\phi(k_n) \propto \mathrm{e}^{-\sigma^2(k_n-k_0)^2} =: c_n$$

  where $\sigma = \Delta x \ll a$, and hence $1/\sigma \gg 1/a$.

- Since
$$k_m - k_n = (m-n)\frac{\pi}{a}$$
we will obtain a "continuous" distribution of states with $|k_n - k_0| < 1/\sigma$ as well as a suppression of other modes.
- Left as an exercise to the student to derive further results about this system.

3.2 Harmonic Oscillator

1/19:

- The harmonic oscillator is one of the most important problems in physics because we can solve it exactly.
- It used to approximate solutions near the bottom of smooth potential wells. It does so via
$$V(x) \approx V(x_0) + \left.\frac{\mathrm{d}V}{\mathrm{d}x}\right|_{x_0}(x-x_0) + \frac{1}{2}\left.\frac{\mathrm{d}^2V}{\mathrm{d}x^2}\right|_{x_0}(x-x_0)^2 + \cdots$$
  - Mathematically, this represents small departures from x_0.
  - Recall that the first derivative goes to zero (because we are at a minimum) and the second one is a constant we can call k, yielding
$$V(x) = V(x_0) + \frac{1}{2}k(x-x_0)^2$$
  - This is now a potential with which we are familiar from classical mechanics.
- Recall what happens in classical mechanics.
  - We get an equation with a second derivative of $u = x - x_0$:
$$m\frac{\mathrm{d}^2u}{\mathrm{d}t^2} = -ku$$
  - This problem is solved in classical mechanics by defining $\omega^2 := k/m$ and solving the differential equation for
$$u = A\sin(\omega t) + B\cos(\omega t)$$
  - From this general solution, we can get to particular solutions using initial conditions.
  - For example, if $u(0) = 0$, then $B = 0$ and
$$u = A\sin(\omega t)$$
  - What happens if we multiply the original equation of motion by $v = \mathrm{d}u/\mathrm{d}t$? We get the conservation of energy!
$$mv\frac{\mathrm{d}v}{\mathrm{d}t} = -ku\frac{\mathrm{d}u}{\mathrm{d}t}$$
$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{mv^2}{2} + \frac{ku^2}{2}\right) = 0$$
  - Note that we associate the left term above with $KE = p^2/2m$ and the right term above with $V(u)$.

- This gives us

$$V(u) = \frac{ku^2}{2} = \frac{k[A\sin(\omega t)]^2}{2} = \frac{kA^2}{2}\sin^2(\omega t)$$
$$K(u) = \frac{mv^2}{2} = \frac{m}{2}\left(\frac{\mathrm{d}}{\mathrm{d}t}[A\sin(\omega t)]\right)^2 = \frac{A^2 m\omega^2}{2}\cos^2(\omega t) = \frac{kA^2}{2}\cos^2(\omega t)$$

  so that

$$V(u) + K(u) = \frac{kA^2}{2}$$

  for all u!

- The situation is different in quantum mechanics.
  - Here, we must begin from

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi_n(x) + \frac{kx^2}{2}\psi_n(x) = E_n\psi_n(x)$$

- What do we know, qualitatively, about a solution to this ODE?
  - Since $V(x)$ is time-independent, the eigenfunctions will be of the form

$$\psi_n(x,t) = \psi_n(x)\mathrm{e}^{-iE_n t/\hbar}$$

  - We will be able to normalize these solutions via

$$\int \mathrm{d}x\, \psi_m^*(x)\psi_n(x) = \delta_{nm}$$

  - The general solution will then be a sum of the normalized solutions, like the following.

$$\psi(x,t) = \sum_n c_n\psi_n(x,t)$$

  - The normalization condition *here* will then yield

$$\sum_n |c_n|^2 = 1$$

  - Lastly, we will be able to calculate expected values, such as

$$\langle\psi|\hat{H}|\psi\rangle = \sum_m |c_m|^2 E_m$$

- We now work toward quantitative solutions $\psi_n(x,t)$, based on insight from the following picture.

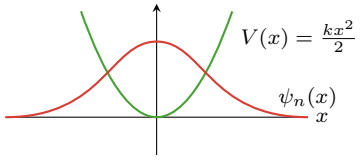


Figure 3.5: Solving the quantum harmonic oscillator with an asymptotic Schrödinger equation.

  - Although it may not be immediately obvious how to solve the Schrödinger equation in this case, we can see from Figure 3.5 that at large values of x, $\psi_n(x) = 0$. Thus, for large x, we will have

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi_n(x) + \frac{kx^2}{2}\psi_n(x) = 0$$

  - This tells us the **asymptotic** behavior of the equation.
- We can then algebraically rearrange this equation into the form

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi_n(x) - \frac{m^2\omega^2x^2}{\hbar^2}\psi_n(x) = 0$$

- To solve it, use an ansatz proportional to the following.

$$\psi_n(x) \propto \exp\Big[-\frac{m\omega}{2\hbar}x^2\Big]$$

  - This works because

$$\frac{\mathrm{d}\psi_n}{\mathrm{d}x} = -\frac{m\omega x}{\hbar}\exp\Big[-\frac{m\omega}{2\hbar}x^2\Big]$$
$$\frac{\mathrm{d}^2\psi_n}{\mathrm{d}x^2} = \left(-\frac{m\omega}{\hbar} + \frac{m^2\omega^2x^2}{\hbar^2}\right)\exp\Big[-\frac{m\omega}{2\hbar}x^2\Big]$$

- In particular, use the ansatz

$$\psi_n(x) = f_n(x)\exp\Big[-\frac{m\omega}{2\hbar}x^2\Big]$$

- Now insert this ansatz into the original equation and solve for values of $f_n(x)$ that give an exact solution.
- Start by calculating that

$$\frac{\mathrm{d}\psi_n}{\mathrm{d}x} = \frac{\mathrm{d}f_n(x)}{\mathrm{d}x}\exp\Big[-\frac{m\omega}{2\hbar}x^2\Big] - f_n(x)\frac{m\omega x}{\hbar}\exp\Big[-\frac{m\omega}{2\hbar}x^2\Big]$$

  and thus

$$\begin{aligned}\frac{\mathrm{d}^2\psi_n}{\mathrm{d}x^2} &= \frac{\mathrm{d}^2f_n(x)}{\mathrm{d}x^2}\exp\Big[-\frac{m\omega}{2\hbar}x^2\Big] - 2\frac{\mathrm{d}f_n(x)}{\mathrm{d}x}\frac{m\omega x}{\hbar}\exp\Big[-\frac{m\omega}{2\hbar}x^2\Big] \\ &\quad - f_n(x)\frac{m\omega}{\hbar}\exp\Big[-\frac{m\omega}{2\hbar}x^2\Big] + f_n(x)\frac{m^2\omega^2x^2}{\hbar^2}\exp\Big[-\frac{m\omega}{2\hbar}x^2\Big] \\ &= \left[f_n''(x) - \frac{2m\omega x}{\hbar}f_n'(x) - f_n(x)\frac{m\omega}{\hbar} + f_n(x)\frac{m^2\omega^2x^2}{\hbar^2}\right]\exp\Big[-\frac{m\omega}{2\hbar}x^2\Big] \\ &= \left[f_n''(x) - \frac{2m\omega x}{\hbar}f_n'(x) + \frac{m\omega}{\hbar}\left(\frac{m\omega x^2}{\hbar} - 1\right)f_n(x)\right]\exp\Big[-\frac{m\omega}{2\hbar}x^2\Big]\end{aligned}$$

- Now we insert the above into the full original Schrödinger equation, cancelling the exponential term immediately to save space.

$$\begin{aligned}-\frac{\hbar^2}{2m}\left[f_n''(x) - \frac{2m\omega x}{\hbar}f_n'(x) + \frac{m\omega}{\hbar}\left(\frac{m\omega x^2}{\hbar} - 1\right)f_n(x)\right] + \frac{m\omega^2x^2}{2}f_n(x) &= E_nf_n(x) \\ -\frac{\hbar^2}{2m}\left(f_n'' - \frac{2m\omega x}{\hbar}f_n' - \frac{m\omega}{\hbar}f_n\right) &= E_nf_n \\ -\frac{\hbar^2}{2m}f_n'' + \hbar\omega x f_n' + \left(\frac{\hbar\omega}{2} - E_n\right)f_n &= 0\end{aligned}$$

- Thus, we have obtained an ODE that we can solve to find particular solutions.
- One obvious solution: the **minimal energy solution**.
- **Minimal energy solution** (to the quantum harmonic oscillator): Take f_n to be a constant C. *Given by*

$$\psi_0(x) = C\exp\Big[-\frac{m\omega}{2\hbar}x^2\Big] \qquad\qquad E_0 = \frac{\hbar\omega}{2}$$

  - Note that it is the above ODE that necessitates $E_0 = \hbar\omega/2$ if f_n is to be a constant.
  - The minimal energy solution classically is zero, but in quantum mechanics, there will always be some energy!
    - Zero energy is impossible because it would imply that the position and momentum are both zero. But there needs to be some uncertainty, in both, so the position and momentum *cannot* both be zero.
    - Essentially, the uncertainty principle *necessitates* a finite nonzero minimal energy. Stated another way, zero energy is *inconsistent* with the uncertainty principle.

- What if we postulate that $f_1 = b_1 x$ for some constant b_1?
  - Then the ODE simplifies to

$$\hbar\omega b_1 x + \left(\frac{\hbar\omega}{2} - E_1\right) b_1 x = 0$$

$$E_1 = \frac{3\hbar\omega}{2}$$

  - Note that

$$E_1 - E_0 = \hbar\omega$$

    - This observation is important because we can actually prove that

$$E_{n+1} - E_n = \hbar\omega$$

      for all $n = 0, 1, 2, \ldots$.
    - We will not prove this in this class, though; we will just postulate it.
    - Essentially, what we do is assume that

$$f_N(x) = \sum_{n=1}^{N} b_n x^n$$

      and solve.
    - All the solutions are either even or odd solutions based on whether N is even or odd. These "even" and "odd" solutions correspond to even and odd polynomial functions.
  - This means that

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$

- In particular, if we let $\xi = x\sqrt{m\omega/\hbar}$, then the solutions f_N are the **Hermite polynomials**.
- **Hermite polynomial**: A polynomial of the following form. *Denoted by* $\boldsymbol{H_n(\xi)}$. *Given by*

$$H_n(\xi) = (-1)^n \exp\left(\xi^2\right) \frac{\mathrm{d}^n}{\mathrm{d}\xi^n}\left[\exp\left(-\xi^2\right)\right]$$

- Thus, the general solutions to the quantum harmonic oscillator

$$\psi_n(x) = \left(\frac{m\omega}{\hbar\pi}\right)^{1/4} \frac{H_n(\xi)}{\sqrt{2^n n!}} \exp\left[-\frac{\xi^2}{2}\right]$$

- On Monday, we will derive this result using **rasing** and **lowering** operators.

3.3 Office Hours (Wagner)

- PSet 2, Q1: Do you want us to rederive the wavefunction, or just answer the questions in the parts?
- Do we have to show our integration steps, or are integral calculators fine?
  - Show whatever we feel comfortable with.
  - Sounds like Wagner thinks we should be able to do all these calculations like we were born doing them, but integral calculators and skipping steps shouldn't lose us any points.
- Including Problem 3 was probably a mistake, but now that it's included, we have to do it.
- PSet 2, Q1d:
  - One way to do this problem is to remember that $\mathrm{d}\langle\hat{r}\rangle/\mathrm{d}t = \langle p\rangle/m$ and $\mathrm{d}\langle p\rangle/\mathrm{d}t = 0$.
  - Now the $\psi = \sum_n c_n \sin(k_n x)$.
  - The mean value of the momentum, once computed explicitly, is

$$\langle p\rangle \propto \int \mathrm{d}x \left[\sum_n c_n \sin(k_n x) \cdot \frac{\partial}{\partial x}\left(\sum_n c_n \sin(k_n x)\right)\right]$$

  - Then we integrate using the trick that

$$\sin x \cos y = \frac{1}{2}\sin(x+y) + \frac{1}{2}\sin(x-y)$$

    - Wagner briefly proves this trig identity.
  - Recall tricks like given an *even* function f,

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

- PSet 2, Q2:
  - There is some part where we do not need to find exact solutions.

3.4 G Chapter 2: Time-Independent Schrödinger Equation

From Griffiths and Schroeter (2018).

Section 2.2: The Infinite Square Well

1/29:

- Goes through the derivation from class.
- The boundary conditions will be justified in Section 2.5!
- Note that since A is complex, normalization technically only determines the magnitude $|A|$. However, the phase of A carries no physical significance, so there is no reason not to choose the simplest solution to $|A|^2 = 2/a$, which is just the positive real square root.
- Notice how, as promised, the TISE delivers a set $\{\psi_n(x)\}$ of solutions!
- **Ground state**: The wave functional solution to the TISE which carries the lowest energy.
- **Excited state**: Any wave functional solution to the TISE that is not the ground state.
- Four properties of the ψ_n of the infinite square well.

1. They are alternately even and odd, with respect to the center of the well.
2. As E_n increases, each successive state has one more **node**.
3. The $\{\psi_n\}$ are mutually orthogonal.
   - Griffiths and Schroeter (2018) proves that any ψ_n, ψ_m $(n \neq m)$ are orthogonal.
4. The $\{\psi_n\}$ are **complete**.

- **Complete** (set of functions): A set of functions such that any other function $f(x)$ can be expressed as a linear combination of them.
  - Griffiths and Schroeter (2018) will not prove the completeness of the functions $\sqrt{2/a}\sin(\pi nx/a)$, but the mathematically inclined student may notice that an infinite sum of these is the **Fourier series** for $f(x)$, and the fact that any function can be expanded in this way is called **Dirichlet's theorem**.
  - To compute the c_n corresponding to an arbitrary f, use **Fourier's trick**:

$$\int \psi_m^*(x) f(x)\,\mathrm{d}x = \sum_{n=1}^{\infty} c_n \int \psi_m^*(x)\psi_n(x)\,\mathrm{d}x = \sum_{c_n} \delta_{mn} = c_m$$

  - Aside (from me): Dirac notation expresses the above statement as simply a consequence of taking the inner product of a vector and a member of the orthonormal basis.

$$\langle \psi_m | f \rangle = c_m$$

- Note on the four properties.
  - Property 1 is true whenever the potential is a symmetric function.
  - Property 2 is universal, regardless of the shape of the potential.
  - Orthogonality is quite general (we'll see exactly how much in Chapter 3).
  - Completeness holds for all potentials we are likely to encounter (but the proofs tend to be nasty).
    - "Most physicists simply *assume* completeness, and hope for the best" (Griffiths & Schroeter, 2018, p. 52).

- With what we know now, we can compute the time evolution of any particle in this system.
  - Simply start with its wave function at $t = 0$, which is $\psi(x, 0)$.
  - Compute expansion coefficients.
  - And take $\psi(x, t)$ to be the sum of stationary states.

- Griffiths and Schroeter (2018) proves — as at the end of class on 1/12 — that $\sum_n |c_n|^2 = 1$ and $\sum_n |c_n|^2 E_n = \langle H \rangle$.

Week 4

Observables and Hermitian Operators

4.1 Harmonic Oscillator: Raising and Lowering Operators

1/22:

- **Raising operator**: The operator defined as follows. *Denoted by* $\hat{\boldsymbol{a}}_+$, $\boldsymbol{a}_+$. *Given by*

$$\hat{a}_+ = \frac{1}{\sqrt{2\hbar m\omega}}[-i\hat{\vec{p}} + m\omega\hat{\vec{x}}]$$

- **Lowering operator**: The operator defined as follows. *Denoted by* $\hat{\boldsymbol{a}}_-$, $\boldsymbol{a}_-$. *Given by*

$$\hat{a}_- = \frac{1}{\sqrt{2\hbar m\omega}}[i\hat{\vec{p}} + m\omega\hat{\vec{x}}]$$

- **Number operator**: The operator defined as follows. *Denoted by* $\boldsymbol{a}_+\boldsymbol{a}_-$. *Given by*

$$a_+a_- = \hat{a}_+ \circ \hat{a}_- = \frac{1}{2\hbar m\omega}\left[\hat{\vec{p}}^2 + m^2\omega^2x^2 - im\omega[\hat{\vec{p}}, \hat{\vec{x}}]\right]$$

- Properties of these operators.
  - We can express $\hat{\vec{p}}, \hat{\vec{x}}$ in terms of a_+, a_- via

$$\hat{\vec{p}} = i\sqrt{\frac{\hbar m\omega}{2}}(\hat{a}_+ - \hat{a}_-) \qquad\qquad \hat{\vec{x}} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}_+ + \hat{a}_-)$$

    - It follows that

$$[\hat{\vec{p}}, \hat{\vec{x}}] = \frac{i\hbar}{2}[a_+ - a_-, a_+ + a_-] = \frac{i\hbar}{2}([a_+, a_-] - [a_-, a_+]) = i\hbar[a_+, a_-]$$

    - Consequently, since $[\hat{\vec{p}}, \hat{\vec{x}}] = -i\hbar$, we have that

$$[a_+, a_-] = -1$$

    - We also have that

$$[a_-, a_+] = 1$$

  - Since $[\hat{\vec{p}}, \hat{x}] = -i\hbar$ and $\omega^2 = k/m$, we have that

$$\begin{aligned} a_+a_- &= \frac{1}{2\hbar m\omega}\left[\hat{\vec{p}}^2 + m^2\omega^2x^2 - m\hbar\omega\right] \\ &= \frac{1}{\hbar\omega}\left[\underbrace{\frac{\hat{\vec{p}}^2}{2m} + \frac{kx^2}{2}}_{\hat{H}} - \frac{\hbar\omega}{2}\right] \\ \hat{H} &= \hbar\omega\left(a_+a_- + \frac{1}{2}\right) \end{aligned}$$

    - Because of the properties of $[a_+, a_-]$ proven above, we similarly have that

$$\hat{H} = \hbar\omega\left(a_- a_+ - \frac{1}{2}\right)$$

    - We can also derive this equation in a manner exactly analogous to the first one.

- How does the number operator act on the eigenstate $|\psi_n\rangle$ of the harmonic oscillator?
  - Since $E_n = \hbar\omega(n + 1/2)$, we have that

$$\begin{aligned}\hbar\omega\left(a_+ a_- + \frac{1}{2}\right)|\psi_n\rangle &= \hat{H}\,|\psi_n\rangle \\ \hbar\omega\left(a_+ a_- + \frac{1}{2}\right)|\psi_n\rangle &= \hbar\omega\left(n + \frac{1}{2}\right)|\psi_n\rangle \\ a_+ a_-\,|\psi_n\rangle &= n\,|\psi_n\rangle\end{aligned}$$

- How do the raising and lowering operators act on the eigenstate $|\psi_n\rangle$ of the harmonic oscillator?
  - Using a number of the above substitutions, we have that

$$\begin{aligned}\hat{H}(a_+\,|\psi_n\rangle) &= \left[\hbar\omega\left(a_+ a_- + \frac{1}{2}\right)\right](a_+\,|\psi_n\rangle) \\ &= \hbar\omega\left(a_+ a_- a_+ + \frac{1}{2}a_+\right)|\psi_n\rangle \\ &= \hbar\omega a_+\left(a_- a_+ + \frac{1}{2}\right)|\psi_n\rangle \\ &= \hbar\omega a_+\left(a_+ a_- + 1 + \frac{1}{2}\right)|\psi_n\rangle \\ &= \hbar\omega a_+\left(n + 1 + \frac{1}{2}\right)|\psi_n\rangle \\ &= E_{n+1}(a_+\,|\psi_n\rangle)\end{aligned}$$

  - This means that $\hat{H}$ acts on $a_+\,|\psi_n\rangle$ the same way it acts on $|\psi_{n+1}\rangle$. In other words, it must be that

$$a_+\,|\psi_n\rangle \propto |\psi_{n+1}\rangle$$

  - Similarly,

$$\hat{H}(a_-\,|\psi_n\rangle) = E_{n-1}(a_-\,|\psi_n\rangle)$$

    so

$$a_-\,|\psi_n\rangle \propto |\psi_{n-1}\rangle$$

  - These actions are why a_+, a_- are called the *raising* and *lowering* operators!
  - We now seek to determine the constants of proportionality.
  - First off, note that a_+ and a_- are adjoints, i.e.,

$$a_+^\dagger = a_-$$

    - See Section 2.3 of Griffiths and Schroeter (2018) for a proof of this fact.
  - Then for a_+, we know that if

$$a_+\,|\psi_n\rangle = c_+\,|\psi_n\rangle$$

then

$$\begin{aligned} c_+^2 &= c_+^2 \langle \psi_{n+1} | \psi_{n+1} \rangle \\ &= \langle c_+ \psi_{n+1} | c_+ \psi_{n+1} \rangle \\ &= \langle a_+ \psi_n | a_+ \psi_n \rangle \\ &= \langle \psi_n | a_+^\dagger a_+ | \psi_n \rangle \\ &= \langle \psi_n | a_- a_+ | \psi_n \rangle \\ &= \langle \psi_n | a_+ a_- + 1 | \psi_n \rangle \\ &= (n+1) \langle \psi_n | \psi_n \rangle \\ &= n+1 \end{aligned}$$

so that, taking square roots,

$$c_+ = \sqrt{n+1}$$

– By the same method — namely

$$c_-^2 = \langle a_- \psi_n | a_- \psi_n \rangle = \langle \psi_n | a_+ a_- | \psi_n \rangle = n$$

we can also learn that

$$c_- = \sqrt{n}$$

– Therefore,

$$a_+ |\psi_n\rangle = \sqrt{n+1}\, |\psi_{n+1}\rangle \qquad\qquad a_- |\psi_n\rangle = \sqrt{n}\, |\psi_{n-1}\rangle$$

– Note that what we have done here to derive this fact is far more slick than working directly with the unintuitive and complicated formal definitions of a_+, a_-.

- Now is a good time to mention a bit more about Dirac notation.
  – A "ket" represents a vector in a Hilbert space, so $|\psi_n\rangle$ demonstrates that we are talking about the wave function as a vector in the abstract linear algebra sense, not as a function $\psi_n : \mathbb{R}^4 \to \mathbb{C}$.
  – A "bra" represents a linear functional on a Hilbert space. In quantum mechanics, the linear functional $\langle \eta |$ is given by

$$\langle \eta | := \int \mathrm{d}^3 \vec{r}\, \eta^*$$

  – Observe that this "functional" does indeed map any $|\psi_n\rangle$ given to it as an argument to a number $\langle \eta | \psi_n \rangle$!

- $|\psi_n\rangle$ can be defined in terms of a_+, $|\psi_0\rangle$, and constants.
  – Observe that since $a_+ |\psi_0\rangle = |\psi_1\rangle$ and $a_+ |\psi_1\rangle = \sqrt{2}\, |\psi_2\rangle$, we have that

$$|\psi_2\rangle = \frac{a_+}{\sqrt{2}} |\psi_1\rangle = \frac{a_+^2}{\sqrt{2}} |\psi_0\rangle$$

  – Similarly,

$$|\psi_3\rangle = \frac{a_+}{\sqrt{3}} |\psi_2\rangle = \frac{a_+^3}{\sqrt{3 \cdot 2}} |\psi_0\rangle$$

  – Generalizing, we have that

$$|\psi_n\rangle = \frac{a_+^n}{\sqrt{n!}} |\psi_0\rangle$$

- Thus, we have that
$$\psi_n(x) = \left(\frac{1}{\sqrt{2\hbar m\omega}}\right)^n \frac{1}{\sqrt{n!}} \left(-\hbar\frac{\mathrm{d}}{\mathrm{d}x} + xm\omega\right)^n \psi_0(x)$$
where we may recall that
$$\psi_0(x) = \left(\frac{m\omega}{\hbar\pi}\right)^{1/4} \mathrm{e}^{-m\omega x^2/2\hbar}$$

- Final observations about the raising and lowering operators.
  - Since $a_- |\psi_0\rangle = 0$ (as we may readily verify by direct computation), we have that
$$\hbar\frac{\mathrm{d}\psi_0}{\mathrm{d}x} + m\omega x\psi_0 = 0$$
  - We also know that
$$\mathrm{d}(\ln(\psi_0)) = -\frac{m\omega}{\hbar}\frac{\mathrm{d}x^2}{2}$$
so
$$\psi_0 \propto \mathrm{e}^{-m\omega x^2/2\hbar}$$
    - What is the point of this line?? What new information does it give us?

- Raising and lowering operators allow us to compute the kinetic and potential energy of the harmonic oscillator.
  - Kinetic energy.
$$\begin{aligned}
\left\langle \psi_n \middle| \frac{\hat{\vec{p}}^2}{2m} \middle| \psi_n \right\rangle &= -\frac{\hbar\omega}{4} \langle\psi_n|(a_+ - a_-)^2|\psi_n\rangle \\
&= -\frac{\hbar\omega}{4} \langle\psi_n|a_+^2 + a_-^2 - a_+a_- - a_-a_+|\psi_n\rangle \\
&= -\frac{\hbar\omega}{4} \big[\underbrace{\langle\psi_n|a_+^2|\psi_n\rangle}_{\propto\langle\psi_n|\psi_{n+2}\rangle} + \underbrace{\langle\psi_n|a_-^2|\psi_n\rangle}_{\propto\langle\psi_n|\psi_{n-2}\rangle} - \underbrace{2\langle\psi_n|a_+a_-|\psi_n\rangle}_{2n\langle\psi_n|\psi_n\rangle} - \underbrace{\langle\psi_n|1|\psi_n\rangle}_{\langle\psi_n|\psi_n\rangle} \big] \\
&= \frac{\hbar\omega}{4}(2n+1) \\
&= \frac{\hbar\omega}{2}\left(n + \frac{1}{2}\right) \\
&= \frac{E_n}{2}
\end{aligned}$$
  - Potential energy.
$$\begin{aligned}
\langle\psi_n|\hat{H}|\psi_n\rangle &= E_n \\
\left\langle \psi_n \middle| \frac{\hat{\vec{p}}^2}{2m} \middle| \psi_n \right\rangle + \left\langle \psi_n \middle| \frac{k\hat{\vec{x}}^2}{2} \middle| \psi_n \right\rangle &= \frac{E_n}{2} + \frac{E_n}{2} \\
\left\langle \psi_n \middle| \frac{k\hat{\vec{x}}^2}{2} \middle| \psi_n \right\rangle &= \frac{E_n}{2}
\end{aligned}$$
  - Implication: In an energy eigenstate, the harmonic oscillator has equal values of kinetic and potential energies!

- Computing more observables.
  - We can show that

$$\langle\psi_n|\hat{\vec{x}}|\psi_n\rangle = \langle\psi_n|\hat{\vec{p}}|\psi_n\rangle = 0 \qquad \langle\psi_n|\hat{\vec{x}}^2|\psi_n\rangle = \frac{\hbar\omega}{k}\left(n+\frac{1}{2}\right) \qquad \langle\psi_n|\hat{\vec{p}}^2|\psi_n\rangle = \hbar\omega m\left(n+\frac{1}{2}\right)$$

- It follows from the above computations and the facts that

$$\Delta x^2 = \langle\psi_n|\hat{\vec{x}}^2|\psi_n\rangle - (\langle\psi_n|\hat{\vec{x}}|\psi_n\rangle)^2 \qquad \Delta p^2 = \langle\psi_n|\hat{\vec{p}}^2|\psi_n\rangle - (\langle\psi_n|\hat{\vec{p}}|\psi_n\rangle)^2$$

that

$$\Delta x^2 \cdot \Delta p^2 = \hbar^2\left(n+\frac{1}{2}\right)^2$$
$$\Delta x \cdot \Delta p = \frac{\hbar}{2}(2n+1)$$

  - Implication: The ground state $\psi_0(x)$ is represented by a Gaussian since in this case, $\Delta x \cdot \Delta p = \hbar/2$.

- Review from last class.
  - Mostly stuff I already wrote down.
  - One new equation formalizing the even/odd solutions:

$$f_n(x) = (-1)^n f_n(-x)$$

  - The first four Hermite polynomials:

$$H_0(\xi) = 1 \qquad H_1(\xi) = 2\xi \qquad H_2(\xi) = 4\xi^2 - 2 \qquad H_3 = 8\xi^3 - 12\xi$$

  - Summary of the characteristics of E_n: The energy is quantized and grows linearly with n in quanta of $\hbar\omega$, and has a minimum value $\hbar\omega/2$.
  - As with other time-independent potentials, the general solution to the Schrödinger equation will be

$$\psi(x,t) = \sum_n c_n\psi_n(x)\mathrm{e}^{-iE_nt/\hbar}$$

where

$$\langle\psi|\hat{H}|\psi\rangle = \sum_n |c_n|^2 E_n$$

4.2 Time Dependence and Coherent States

1/24:

- Review of the harmonic oscillator.
  - Our Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{kx^2}{2} = \frac{\hat{\vec{p}}^2}{2m} + \frac{k\hat{\vec{x}}^2}{2}$$

    - We have an analogy with the classical $\omega^2 = k/m$.
  - Under this Hamiltonian, $\hat{H}\,|\psi_n\rangle = E_n\,|\psi_n\rangle$ implies that

$$E_n = \hbar\omega\left(\frac{1}{2}+n\right)$$

  - The raising and lowering operators are given by

$$a_+ = \frac{1}{\sqrt{2\hbar m\omega}}[-i\hat{\vec{p}} + m\omega\hat{\vec{x}}] \qquad a_- = \frac{1}{\sqrt{2\hbar m\omega}}[i\hat{\vec{p}} + m\omega\hat{\vec{x}}]$$

- Together, these imply that
$$\hat{H} = \hbar\omega\left(a_+a_- + \frac{1}{2}\right)$$
- We also have that
$$a_+a_-\left|\psi_n\right\rangle = n\left|\psi_n\right\rangle \qquad a_+\left|\psi_n\right\rangle = \sqrt{n+1}\left|\psi_{n+1}\right\rangle$$
$$[a_-, a_+] = 1 \qquad a_-\left|\psi_n\right\rangle = \sqrt{n}\left|\psi_{n-1}\right\rangle$$
- We call a_+a_- the number operator.
- We should go home and learn these formulas.

– The full eigenstate is
$$\psi(x,t) = \sum_{n=0}^{\infty} \underbrace{c_n\psi_n(x)\mathrm{e}^{-iE_nt/\hbar}}_{\psi_n(x,t)}$$

– Two properties of this eigenstate.

1. We have that
$$\left|\psi\right\rangle = \sum_{n=0}^{\infty} c_n\mathrm{e}^{-iE_nt/\hbar}\left|\psi_n\right\rangle$$
which implies that
$$\sum_{n=0}^{\infty}\left|c_n\right|^2 = 1$$
since $\langle\psi|\psi\rangle = 1$ and $\langle\psi_n|\psi_m\rangle = \delta_{nm}$.
2. We have that
$$\langle\psi|\hat{H}|\psi\rangle = \sum_{n=0}^{\infty}|c_n|^2E_n$$

– We have that
$$\left\langle\psi_n\left|\frac{k\hat{\vec{x}}^{\,2}}{2}\right|\psi_n\right\rangle = \frac{\hbar\omega}{2}\left(n+\frac{1}{2}\right) = \frac{E_n}{2} \qquad \left\langle\psi_n\left|\frac{\hat{\vec{p}}^{\,2}}{2m}\right|\psi_n\right\rangle = \frac{\hbar\omega}{2}\left(n+\frac{1}{2}\right) = \frac{E_n}{2}$$
- Note that this makes sense because the sum $E_n/2 + E_n/2$ of potential and kinetic should be E_n, and it will be!

– Additionally, recall that we have
$$\hat{\vec{p}}^{\,2} \propto (a_+ - a_-)^2 \qquad \hat{\vec{x}}^{\,2} \propto (a_+ + a_-)^2$$
- Thus, we have that
$$\langle\psi_n|\hat{\vec{p}}|\psi_n\rangle = \langle\psi_n|(a_+ - a_-)|\psi_n\rangle = 0 \qquad \langle\psi_n|\hat{\vec{x}}|\psi_n\rangle = \langle\psi_n|(a_+ + a_-)|\psi_n\rangle = 0$$

– The harmonic oscillator is a very important problem in physics, and we should know it by heart! (In order to pass the class.)

- Recall as well that there is a correspondence between the Dirac notation and the functional notation, given by
$$\psi_n(x) \mapsto \left|\psi_n\right\rangle$$

– As an additional example,
$$\frac{1}{\sqrt{2\hbar m\omega}}\left[-\hbar\frac{\mathrm{d}}{\mathrm{d}x} + m\omega x\right]\psi_n(x) = \sqrt{n+1}\psi_{n+1}(x) \quad \mapsto \quad a_+\left|\psi_n\right\rangle = \sqrt{n+1}\left|\psi_{n+1}\right\rangle$$

- One more example:

$$\hbar\frac{\mathrm{d}\psi_0}{\mathrm{d}x} + m\omega x\psi_0(x) = 0 \quad \mapsto \quad a_-\left|\psi_0\right\rangle = 0$$

  - Note that solving this ODE yields the solution

$$\psi_0 = C\exp\left(-\frac{m\omega x^2}{2\hbar}\right)$$

  - It appears that this is how we intuitively derive the ansatz we used last Friday!

- Now we start on some new content.
- Observe that

$$\frac{2m\omega\hat{\vec{x}}}{\sqrt{2\hbar m\omega}} = a_+ + a_-$$
$$\hat{\vec{x}} = \sqrt{\frac{\hbar}{2m\omega}}(a_+ + a_-)$$

- In classical mechanics, the solution to the harmonic oscillator is

$$x(t) = A\sin\omega t + B\cos\omega t$$

- We now investigate the observables of $|\psi\rangle$.
- To start with, we show how $\langle\psi|\hat{\vec{x}}|\psi\rangle$ varies with time. This will lead into a discussion of something called coherent states. Let's begin.
  - We start with

$$\langle\psi|\hat{\vec{x}}|\psi\rangle = \sum_{m,n=0}^{\infty} c_m^* c_n \mathrm{e}^{i(E_m-E_n)t/\hbar}\langle\psi_m|\hat{\vec{x}}|\psi_n\rangle$$

  - We can algebraically manipulate the above to

$$\begin{aligned}
\langle\psi|\hat{\vec{x}}|\psi\rangle &= \sum_{m,n=0}^{\infty} c_m^* c_n \mathrm{e}^{i(\hbar\omega(m-n))t/\hbar}\sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n+1}\delta_{m,n+1} + \sqrt{n}\delta_{m,n-1}\right)\\
&= \sum_{n=0}^{\infty} c_{n+1}^* c_n \mathrm{e}^{i\omega t}\sqrt{\frac{\hbar}{2m\omega}}\sqrt{n+1} + \sum_{n=1}^{\infty} c_{n-1}^* c_n \mathrm{e}^{-i\omega t}\sqrt{\frac{\hbar}{2m\omega}}\sqrt{n}\\
&= \sum_{n=0}^{\infty} c_{n+1}^* c_n \mathrm{e}^{i\omega t}\sqrt{\frac{\hbar}{2m\omega}}\sqrt{n+1} + \sum_{n=0}^{\infty} c_n^* c_{n+1} \mathrm{e}^{-i\omega t}\sqrt{\frac{\hbar}{2m\omega}}\sqrt{n+1}\\
&= \sqrt{\frac{\hbar}{2m\omega}}\cos(\omega t)\left[\sum_{n=0}^{\infty}\left(c_{n+1}^* c_n + c_n^* c_{n+1}\right)\sqrt{n+1}\right]\\
&\quad + \sqrt{\frac{\hbar}{2m\omega}}\sin(\omega t)\left[\sum_{n=0}^{\infty}\left(c_{n+1}^* c_n - c_n^* c_{n+1}\right)\sqrt{n+1}\right]
\end{aligned}$$

  - Thus,

$$\langle\psi|\hat{\vec{x}}|\psi\rangle = A\cos\omega t + B\sin\omega t$$

  where

$$\begin{aligned}
A &= 2\,\mathrm{Re}\left[\sum_{n=0}^{\infty} c_{n+1}^* c_n\sqrt{n+1}\right]\sqrt{\frac{\hbar}{2m\omega}} & B &= 2\,\mathrm{Im}\left[\sum_{n=0}^{\infty} c_{n+1}^* c_n\sqrt{n+1}\right]\sqrt{\frac{\hbar}{2m\omega}}\\
&= \mathrm{Re}\left[\sum_{n=0}^{\infty} c_{n+1}^* c_n\sqrt{n+1}\right]\sqrt{\frac{2\hbar}{m\omega}} & &= \mathrm{Im}\left[\sum_{n=0}^{\infty} c_{n+1}^* c_n\sqrt{n+1}\right]\sqrt{\frac{2\hbar}{m\omega}}
\end{aligned}$$

– Now for large values of n,

$$\sqrt{n+1}\sqrt{\frac{2\hbar}{m\omega}} = \sqrt{\frac{2\hbar\omega(n+1)}{m\omega^2}} \approx \sqrt{\frac{2E_n}{m\omega^2}}$$

where

$$E_n = \hbar\omega\left(n+\frac{1}{2}\right) \qquad x = A\sin\omega t \qquad E = \frac{m\omega^2 A^2}{2} \qquad A = \sqrt{\frac{2E}{m\omega^2}}$$

■ How can we just ignore the real and imaginary sum terms??

– Now take the harmonic oscillator. Notice that $\sum_n$ is dominated by large values of $n \approx \bar{n}$, close to $\bar{n}$, where $\bar{n} \gg 1$. Thus,

$$\langle\psi|\hat{\vec{x}}|\psi\rangle = \sqrt{\frac{2E\bar{n}}{m\omega^2}}\sum_{n=0}^{\infty}\mathrm{Re}\left[\sum c_{n+1}^* c_n\right]\sin\omega t$$

and

$$\langle\psi|\hat{\vec{x}}^{\,2}|\psi\rangle - (\,\langle\psi|\hat{\vec{x}}|\psi\rangle)^2 \neq 0$$

– This is *not* classical motion.

– The states that come closest to realizing classical motion are called **coherent states**.

- **Coherent state** (of the harmonic oscillator): A state in which the uncertainty in $\hat{x}$ is minimized. *Denoted by* $|\boldsymbol{\alpha}\rangle$.
- It turns out that the coherent states of the harmonic oscillator are the eigenstates of the lowering operator. Denoting the corresponding eigenvalue by α, we have that

$$a_-\,|\alpha\rangle = \alpha\,|\alpha\rangle$$

- Aside: $|\alpha\rangle$ can surely be expressed as a linear combination of the ψ_n. What does the lowering operator do to ψ_0, in particular, should it have a nonzero coefficient?

  – It acts as follows, simply zeroing it out.

$$a_-\,|\psi_0\rangle = 0\,|\psi_0\rangle$$

- Now what is $|\alpha\rangle$?
- Well, for a state to be coherent, we must have

$$\begin{aligned}\frac{\hbar}{2} &= \sigma_x^2 \\ &= \langle\alpha|\hat{\vec{x}}^{\,2}|\alpha\rangle - (\,\langle\alpha|\hat{\vec{x}}|\alpha\rangle)^2 \\ &= \frac{\hbar}{2m\omega}\left[\,\langle\alpha|(a_+ + a_-)^2|\alpha\rangle - (\,\langle\alpha|(a_+ + a_-)|\alpha\rangle)^2\right] \\ &= \frac{\hbar}{2m\omega}\left[\,\langle\alpha|a_+^2 + a_+a_- + a_-a_+ + a_-^2|\alpha\rangle - (\,\langle\alpha|(a_+ + a_-)|\alpha\rangle)^2\right] \\ &= \ldots\end{aligned}$$

  – We'll finish this up next time.

  – Is it really $\hbar/2$ here??

4.3 Hermitian Operators; Position and Momentum Eigenstates

1/26:

- Recap of the harmonic oscillator.
  - The Hamiltonian (in terms of $\hat{p}, \hat{x}$; and in terms of a_+, a_-).
  - The definitions of a_+, a_-.
  - The effect of a_+, a_- on $|n\rangle := |\psi_n\rangle$.
  - The effect of $\hat{H}$ on $|n\rangle$.
  - Adjoints of the **ladder operators**:

$$(a_+)^\dagger = a_- \qquad\qquad (a_-)^\dagger = a_+$$

  - The commutator $[a_-, a_+] = 1$.
  - The formula for a generic state $|\psi\rangle$, i.e.,

$$|\psi\rangle = \sum_{n=0}^{\infty} c_n \mathrm{e}^{-iE_n t/\hbar} |n\rangle$$

    - This will of course appear as a question in the midterm and final!
    - We must also remember that

$$1 = \langle\psi|\psi\rangle = \sum_{n=0}^{\infty} |c_n|^2 \qquad\qquad 1 = \langle\psi|\hat{H}|\psi\rangle = \sum_{n=0}^{\infty} |c_n|^2 E_n$$

  - The probability of measuring the energy of $|\psi\rangle$ as E_n is $|c_n|^2$.
    - So when we perform a measurement, the energy of $|\psi\rangle$ collapses to that of one eigenstate.
- **Ladder operator**: An element in the class of operators that send $|n\rangle$ to scalar multiples of $|n+i\rangle$ for some $i \in \mathbb{Z} \setminus \{0\}$.
  - The raising and lowering operators are ladder operators!
- The midterm.
  - 50% of the midterm will be related to harmonic oscillator content, esp. the last few equations above following the definition of $|\psi\rangle$.
  - The midterm will only cover what we covered through today.
  - The midterm may be on February 5. It sounds like it will be on Friday, February 9, though.
  - It will take place in this classroom.
  - It will be open book.
    - Can we bring virtual notes, or does everything have to be printed out??
  - The midterm questions will be the same level as the PSet questions; there may even be some repetition! Def take a look at the PSets.
  - PSet 1 through PSet 4 will be covered on the midterm.
  - Foundations of quantum mechanics plus one-dimensional problems.
  - We will be allowed to turn in the midterm through 1:00 PM, though it shouldn't take us more than 50 minutes.
- The first two problems of PSet 4 must be solved; the third one can be dropped *or* can be solved for 5 bonus points.
- We now begin on new content.

- Recall the following expression from last class.

$$\langle\psi|\hat{\vec{x}}|\psi\rangle = \sqrt{\frac{2\hbar}{m\omega}}\sum_{n=0}^{\infty}\left[\sqrt{n+1}\cos(\omega t)\,\mathrm{Re}(c_{n+1}^{*}c_n) + \sqrt{n+1}\sin(\omega t)\,\mathrm{Im}(c_{n+1}^{*}c_n)\right]$$

  - This is a really complicated expression, especially as we prepare to talk about coherent states.
  - Thus, it was quite difficult to prove that

$$\langle\psi|\hat{\vec{x}}^{\,2}|\psi\rangle \neq (\,\langle\psi|\hat{\vec{x}}|\psi\rangle)^2$$

  - Can we introduce a notation that will allow us to work with this expression and similar ones more easily?

- Wagner restates the definition of a coherent state and and the uncertainty principles.

- Recall that

$$a_-\,|\alpha\rangle = \alpha\,|\alpha\rangle$$

  and that

$$|\alpha\rangle = \sum_n c_n\,|n\rangle$$

- The Hermitian conjugate of a_- is a_+ and hence, the Hermitian conjugate of $a_-\,|\alpha\rangle$ is

$$\langle\alpha|\,a_+ = \langle\alpha|\,\alpha^*$$

- Thus, since $\langle\alpha|\alpha\rangle = 1$

$$\langle\alpha|a_+a_-|\alpha\rangle = \alpha\,\langle\alpha|a_+|\alpha\rangle = \alpha\,\langle\alpha|\alpha^*|\alpha\rangle = \alpha^*\alpha\,\langle\alpha|\alpha\rangle = \alpha^*\alpha$$

- We now seek to verify that an eigenstate of a_- does, in fact, minimize the uncertainty in $\hat{x}$.
  - For simplicity, we will consider $|\alpha\rangle$ at $t = 0$ (this will remove the complex exponential from calculations).
  - First off, we have that

$$\langle\alpha|\hat{\vec{x}}|\alpha\rangle = \sqrt{\frac{\hbar}{2m\omega}}\,\langle\alpha|(a_+ + a_-)|\alpha\rangle = (\alpha^* + \alpha)\sqrt{\frac{\hbar}{2m\omega}}$$

    and

$$\begin{aligned}
\langle\alpha|\hat{\vec{x}}^{\,2}|\alpha\rangle &= \frac{\hbar}{2m\omega}\,\langle\alpha|(a_+ + a_-)(a_+ + a_-)|\alpha\rangle \\
&= \frac{\hbar}{2m\omega}[\,\langle\alpha|a_+^2|\alpha\rangle + \,\langle\alpha|a_+a_-|\alpha\rangle + \,\langle\alpha|a_-a_+|\alpha\rangle + \,\langle\alpha|a_-^2|\alpha\rangle] \\
&= \frac{\hbar}{2m\omega}[(\alpha^*)^2\underbrace{\langle\alpha|\alpha\rangle}_{1} + \alpha^*\alpha + \,\langle\alpha|(\underbrace{a_-a_+ - a_+a_-}_{1} + a_+a_-)|\alpha\rangle + \alpha^2] \\
&= \frac{\hbar}{2m\omega}[(\alpha^*)^2 + \alpha^2 + 2|\alpha|^2 + 1]
\end{aligned}$$

  - Combining these, we have that

$$\langle\alpha|\hat{\vec{x}}^{\,2}|\alpha\rangle - (\,\langle\alpha|\hat{\vec{x}}|\alpha\rangle)^2 = \frac{\hbar}{2m\omega}[(\alpha^*)^2 + \alpha^2 + 2|\alpha|^2 + 1 - (\alpha^*)^2 - \alpha^2 - 2|\alpha|^2] = \frac{\hbar}{2m\omega}$$

– Second, we have that

$$\langle\alpha|\hat{\vec{p}}|\alpha\rangle = \sqrt{\frac{\hbar m\omega}{2}}\,\langle\alpha|(a_+ - a_-)|\alpha\rangle = \sqrt{\frac{\hbar m\omega}{2}}(\alpha^* - \alpha)$$

and

$$\begin{aligned}\langle\alpha|\hat{\vec{p}}^2|\alpha\rangle &= -\frac{\hbar m\omega}{2}\,\langle\alpha|(a_+ - a_-)(a_+ - a_-)|\alpha\rangle \\ &= -\frac{\hbar m\omega}{2}\big[(\alpha^*)^2 + \alpha^2 - |\alpha|^2 - \langle\alpha|\underbrace{a_-a_+}_{a_+a_-+1}|\alpha\rangle\big] \\ &= -\frac{\hbar m\omega}{2}\left[(\alpha^*)^2 + \alpha^2 - 2|\alpha|^2 - 1\right]\end{aligned}$$

– Combining these, we have that

$$\langle\alpha|\hat{\vec{p}}^2|\alpha\rangle - (\,\langle\alpha|\hat{\vec{p}}|\alpha\rangle)^2 = \frac{\hbar m\omega}{2}\left[-(\alpha^*)^2 - \alpha^2 + 2|\alpha|^2 + 1 + (\alpha^*)^2 + \alpha^2 - 2|\alpha|^2\right] = \frac{\hbar m\omega}{2}$$

– Therefore,

$$\begin{aligned}\sigma_p^2\sigma_x^2 &= \frac{\hbar m\omega}{2}\cdot\frac{\hbar}{2m\omega} \\ &= \frac{\hbar^2}{4} \\ \sigma_p\sigma_x &= \frac{\hbar}{2}\end{aligned}$$

as desired.

- If we reassert full time dependence, we obtain

$$|\alpha\rangle\,(t) = \sum_n c_n \mathrm{e}^{-iE_nt/\hbar}\,|n\rangle$$

– Then

$$\begin{aligned}a_-\,|\alpha\rangle &= \sum_{n=0}^{\infty} c_n \mathrm{e}^{-iE_nt/\hbar}\sqrt{n}\,|n-1\rangle \\ &= \sum_{n=0}^{\infty} c_{n+1}\mathrm{e}^{-iE_{n+1}t/\hbar}\sqrt{n+1}\,|n\rangle\end{aligned}$$

– And recall that

$$a_-\,|\alpha\rangle = \alpha\,|\alpha\rangle$$

– Thus, via term-by-term transitivity for each $|n\rangle$,

$$\begin{aligned}\alpha c_n &= c_{n+1}\mathrm{e}^{-i(E_{n+1}-E_n)t/\hbar}\sqrt{n+1} \\ \alpha c_n &= c_{n+1}\mathrm{e}^{-i\omega t}\sqrt{n+1}\end{aligned}$$

– We can continue on with this recurrence relation to find a formula for all coefficients c_n, from which we can define $|\alpha\rangle$ explicitly as a linear combination of the $|n\rangle$.

- If α is real and $\psi_\alpha(x)$ denotes the time-independent factor in $|\alpha\rangle$, then

$$\begin{aligned}a_-\psi_\alpha(x) &= \alpha\psi_\alpha(x) \\ \left[\hbar\frac{\mathrm{d}}{\mathrm{d}x} + m\omega x\right]\psi_\alpha(x) &= \alpha\psi_\alpha(x)\end{aligned}$$

  - Then
$$\frac{1}{\psi_\alpha}\frac{\mathrm{d}}{\mathrm{d}x}\psi_\alpha + \left(\frac{m\omega x}{\hbar} - \alpha\right) = 0$$
  - Thus, solving the differential equation, we obtain
$$\psi_\alpha = \exp\left[-\frac{m\omega}{2\hbar}(x - \langle x\rangle)^2\right]$$
    which is a Gaussian.
  - Therefore,
$$a_- |0\rangle = 0\,|0\rangle$$

- We will program the time evolution of a coherent state in Python or Mathematica??
  - A real wave function is a crazy thing that does flip from side to side at $T/2$ and T.
    - Essentially,
$$|\psi(x,t)|^2 = |\psi(-x, t + T/2)|^2$$
  - A coherent state is just a Gaussian that oscillates back and forth to both sides of the y-axis.

4.4 G Chapter 2: Time-Independent Schrödinger Equation

From Griffiths and Schroeter (2018).

Section 2.3: The Harmonic Oscillator

1/29:
- Sets up the relevant TISE, as in class.
- Note that "it is customary to eliminate the spring constant in favor of the classical frequency" (Griffiths & Schroeter, 2018, p. 58).
- Goes through the ladder operator method in great detail and very coherently; I should probably return!!
  - There is a proof in here of why $a_+^\dagger = a_-$.
- Goes through the **power series method** from the Lecture 7 notes.
  - This is the brute force method, though it is useful (as with the hydrogen atom later on).
- **Canonical commutation relation**: The relation defined as follows. *Given by*
$$[\hat{x}, \hat{\vec{p}}] = i\hbar$$

Section 2.4: The Free Particle

- Relevant to 1/5 and 1/17 discussions; I should probably return!!

Section 2.5: The Delta-Function Potential

- Relevant to PSet 2; I should probably return!!

Section 2.6: The Finite Square Well

- Relevant to PSet 2; I should probably return!!

4.5 G Chapter 3: Formalism

From Griffiths and Schroeter (2018).

Section 3.1: Hilbert Space

- Purpose: Recast some of the miracles we've encountered thus far in more powerful terms.

1/9:
- **Square-integrable** (function): A function $f : \mathbb{C} \to \mathbb{C}$ satisfying the following condition. *Constraint*

$$\int_a^b |f(x)|^2 \, \mathrm{d}x < \infty$$

1/29:
- Lots of stuff I should read just for fun (tons of answers to questions I've wondered at over the years), and some stuff actually related to in-class discussions of Hermitian operators, compatible operators, proving the uncertainty principle, Gaussian wave packets, the Ehrenfest theorem, Dirac notation, etc.

4.6 G Appendix: Linear Algebra

From Griffiths and Schroeter (2018).

- A terrific review of relevant concepts, all expressed in Dirac notation.

4.7 T Chapter 7: The One-Dimensional Harmonic Oscillator

From Townsend (2012).

Section 7.7: Time Dependence

- There is some stuff here on $|\psi(x,t)|^2 = |\psi(-x, t + T/2)|^2$.

Section 7.8: Coherent States

- **Coherent state**: A superposition of energy eigenstates of the harmonic oscillator that is also an eigenstate of the lowering operator. *Denoted by* $\boldsymbol{|\alpha\rangle}$.
- $\boldsymbol{\alpha}$: The eigenvalue corresponding to the coherent state $|\alpha\rangle$.
  - Since a_- is not Hermitian, α need not be real.
- Coherent states "come closest to representing classical electromagnetic waves with a well-defined phase" (Townsend, 2012, p. 263).
  - For a harmonic oscillator, they come "closest to the classical limit of a particle oscillating back and forth in a harmonic oscillator potential" (Townsend, 2012, p. 263).
- Coherent states were first derived by Schrödinger when he was looking for solutions to the Schrödinger equation that satisfy the **correspondence principle**.
- **Correspondence principle**: The behavior of systems described by the theory of quantum mechanics reproduces classical physics in the limit of large quantum numbers.
- Townsend (2012) completes Wagner's derivation of $|\alpha\rangle$ as a linear combination of the $|n\rangle$.
- Time Evolution of a Coherent State.
- Repeat of the derivation of the minimum uncertainty from class.
- Shows that the ground coherent state is an oscillating Gaussian.

4.8 L Section 23: The Linear Oscillator

From Landau and Lifshitz (1977).

- The solution to Problem 3 has Schrödinger's derivation of which wave functions minimize the uncertainty relation.

Week 5

Three-Dimensional Systems

5.1 Three-Dimensional Problems

1/29:

- 3D problems still solve the Schrödinger equation, just in 3D.

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

  - Slightly more complicated here, but not too much.

- Focus: Time-independent potentials for now, that is

$$V(\vec{r},t) = V(\vec{r})$$

  - 3D time-independent potentials still allow us to split the wave function as on the left below, and we also still seek energy eigenvalues of the system on the right below.

$$\psi(\vec{r},t) = \psi(\vec{r})\cdot\phi(t) \qquad\qquad -\frac{\hbar^2}{2m}\vec{\nabla}^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r})$$

  - These two facts still imply that the solution will be of the form

$$\psi(\vec{r},t) = \psi(\vec{r})\mathrm{e}^{-iEt/\hbar}$$

    - No difference between 1D and 3D!

- So 1D and 3D are remarkably similar. But where do they differ?

- Example: In 3D, there will be 3 components of the momentum, given as follows.

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \qquad \hat{p}_y = -i\hbar\frac{\partial}{\partial y} \qquad \hat{p}_z = -i\hbar\frac{\partial}{\partial z}$$

  - Note that these three momenta commute as follows.

$$[\hat{p}_x,\hat{p}_y] = [\hat{p}_y,\hat{p}_z] = [\hat{p}_z,\hat{p}_x] = 0$$

- Example: 3 components of the position, also commutative.

$$[\hat{x},\hat{y}] = [f(\hat{x}),f(\hat{y})] = [f(\hat{x}),g(\hat{x})] = [f(\hat{x}),g(\hat{z})] = 0$$

  - As in PSet 4, f, g are arbitrary real functions of the operator.

- The only commutators that are not zero are those we obtained before, e.g.,

$$[\hat{p}_x, \hat{x}] = -i\hbar \qquad [\hat{\vec{p}}, V(\vec{r})] = -i\hbar\vec{\nabla}V(\vec{r})$$

  - Recall that we still have

$$[\hat{p}_x, \hat{y}] = [\hat{p}_x, \hat{z}] = 0 \qquad [V(\vec{r}), \hat{\vec{r}}] = 0$$

- In the presence of $V(\vec{r})$, neither of $\hat{\vec{p}}, \hat{x}$ are conserved quantities. We know this because

$$[\hat{H}, \vec{p}] = [\hat{H}, \vec{r}] \neq 0$$

- In an atom...
  - Potential is only a function of the *magnitude* of distance from the nucleus. Mathematically,

$$V(\vec{r}) = V(r)$$

  - Likewise, angular momentum $\vec{L} = \vec{r} \times \vec{p}$ is conserved. Here's why:
    - Recall that

$$\begin{aligned}\frac{\mathrm{d}\vec{L}}{\mathrm{d}t} &= \frac{\mathrm{d}\vec{r}}{\mathrm{d}t} \times \vec{p} + \vec{r} \times \frac{\mathrm{d}\vec{p}}{\mathrm{d}t} \\ &= \frac{1}{m}\underbrace{\vec{p} \times \vec{p}}_{0} + \vec{r} \times \underbrace{\frac{\mathrm{d}\vec{p}}{\mathrm{d}t}}_{-\vec{\nabla}V(r)}\end{aligned}$$

    - Working with the second term a bit more, we have that

$$\begin{aligned}\vec{\nabla}V(r) &= \vec{x}\frac{\partial V}{\partial x} + \vec{y}\frac{\partial V}{\partial y} + \vec{z}\frac{\partial V}{\partial z} \\ &= \vec{x}\left(\frac{\partial V}{\partial r}\frac{\partial r}{\partial x}\right) + \vec{y}\left(\frac{\partial V}{\partial r}\frac{\partial r}{\partial y}\right) + \vec{z}\left(\frac{\partial V}{\partial r}\frac{\partial r}{\partial z}\right) \\ &= \frac{\partial V}{\partial r}\left(\vec{x}\frac{\partial r}{\partial x} + \vec{y}\frac{\partial r}{\partial y} + \vec{z}\frac{\partial r}{\partial z}\right)\end{aligned}$$

      - ➢ Taking the cross product of the above (evaluated at $r = \sqrt{x^2 + y^2 + z^2}$) with $\vec{r}$ yields zero.
      - ➢ Alternatively, we may observe that like each $\partial V/\partial x \propto x$, we have $\vec{\nabla}V \propto \vec{r}$ for a central potential (just picture it), and therefore the cross product of $\vec{r}$ and a vector proportional to $\vec{r}$ will be zero.
    - Therefore,

$$\frac{\mathrm{d}\vec{L}}{\mathrm{d}t} = \frac{1}{m}\underbrace{\vec{p} \times \vec{p}}_{0} + \underbrace{\vec{r} \times c\vec{r}}_{0} = 0$$

      so angular momentum is conserved, as desired.

- What does it mean that these two quantities are conserved?
  - It means that when we take the classical Hamiltonian

$$\hat{H} = \frac{\vec{p}^{\,2}}{2m} + V(r)$$

    we can separate it into a radial and a perpendicular component so that

$$\begin{aligned}\hat{H} &= \frac{\hat{p}_r^2}{2m} + \frac{\hat{p}_\perp^2}{2m} + V(r) \\ &= \frac{\hat{p}_r^2}{2m} + \underbrace{\frac{\vec{L}^2}{2mr^2} + V(r)}_{V_{\text{eff}}(r)}\end{aligned}$$

- Here's why we can make the above algebraic manipulations.
  - To begin, we can always split the momentum operator into radial and perpendicular components.
  - We also know, since $\vec{p}_\perp$ and $\vec{r}$ are perpendicular, that
$$\vec{L}^2 = (\vec{p}_\perp \times \vec{r})^2 = [p_\perp r \sin(90°)]^2 = p_\perp^2 r^2 = \hat{p}_\perp^2 r^2$$
  - However, it is the conservation of angular momentum, in particular, which implies that $\vec{L}^2$ is a constant, and hence that making the substitution $\hat{p}_\perp^2 = \vec{L}^2/r^2$ will allow the sum of the second two terms to be *purely* a function of r (as opposed to, per se, a function of r and $\vec{L}$).
- What is the implication of this effective potential?

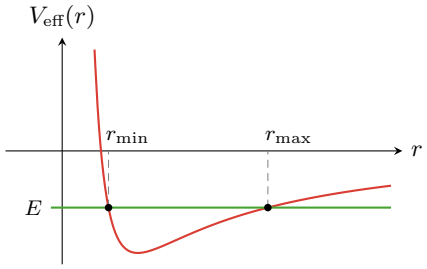


Figure 5.1: Effective potential.

  - Consider the classical case of planetary motion with
$$V_{\text{eff}}(r) = -\frac{GM_0 m}{r} + \frac{\vec{L}^2}{2mr^2}$$
  - Given a total energy E for the system, the planets dance between an r_{min} and r_{max}.
  - This gives the elliptical planetary motion.
  - Of course, we will not deal with planetary motion in this course, but we will deal with something very similar called the **hydrogen atom**.
- We now investigate some analogies and differences between classical and quantum mechanics.
- Before we begin, a quick aside on some commutator rules will be useful.
  1. $[\hat{A}^2, \hat{B}] = \hat{A}[\hat{A}, \hat{B}] + [\hat{A}, \hat{B}]\hat{A}$.
     Proof.
$$\begin{aligned}[\hat{A}^2, \hat{B}] &= \hat{A}^2\hat{B} - \hat{B}\hat{A}^2 \\ &= \hat{A}(\hat{A}\hat{B} - \hat{B}\hat{A}) + (\hat{A}\hat{B} - \hat{B}\hat{A})\hat{A} \\ &= \hat{A}[\hat{A}, \hat{B}] + [\hat{A}, \hat{B}]\hat{A}\end{aligned}$$
     □
  2. $[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}$.
  3. $[\hat{A}, \hat{B}\hat{C}] = \hat{B}[\hat{A}, \hat{C}] + [\hat{A}, \hat{B}]\hat{C}$.
  4. Bilinearity, i.e.,
$$[\hat{A} + \hat{B}, \hat{C}] = [\hat{A}, \hat{C}] + [\hat{B}, \hat{C}] \qquad [c\hat{A}, \hat{B}] = c[\hat{A}, \hat{B}]$$
$$[\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}] \qquad [\hat{A}, c\hat{B}] = c[\hat{A}, \hat{B}]$$
- None of these rules is trivial, but they can all be demonstrated by expanding as with the first rule.

- So getting back to it, the analogies and differences we will prove are...
  1. The quantum angular momentum is conserved directionally and overall;
  2. The square of the quantum angular momentum is conserved;
  3. The quantum angular momentum *cannot* be determined to infinite precision in more than one direction simultaneously;
  4. The square of the quantum angular momentum and the quantum angular momentum can be determined to infinite precision simultaneously.
- Task 1: To prove that the quantum angular momentum is conserved directionally, we will show that the angular momentum in different directions commutes with the Hamiltonian. To prove that it is conserved overall, we will add the previous three results. Let's begin.
  - Mathematically, we want to determine

$$[\hat{H}, \hat{L}_i] \stackrel{?}{=} 0$$

    since if $[\hat{H}, \hat{L}_i] = 0$, then

$$\frac{\mathrm{d}}{\mathrm{d}t}\Big(\langle\psi|\hat{L}_i|\psi\rangle \Big) = \frac{i}{\hbar} \langle\psi|\underbrace{[\hat{H}, \hat{L}_i]}_{0}|\psi\rangle = 0$$

  - Let's start with $\hat{L}_x$.
  - Since

$$\vec{L} = \vec{r} \times \vec{p} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = \hat{x}(yp_z - p_y z) + \hat{y}(p_x z - p_z x) + \hat{z}(xp_y - p_x y)$$

    we know that

$$\hat{L}_x = yp_z - p_y z$$

  - Additionally, recall that

$$\hat{H} = \frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2m} + V(r)$$

  - Thus, we have that

$$\begin{aligned}
[\hat{H}, \hat{L}_x] &= \left[\frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2m} + V(r), \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \right] \\
&= \left[\frac{\hat{p}_x^2}{2m}, \hat{y}\hat{p}_z \right] + \left[\frac{\hat{p}_y^2}{2m}, \hat{y}\hat{p}_z \right] + \left[\frac{\hat{p}_z^2}{2m}, \hat{y}\hat{p}_z \right] \\
&\quad + \left[\frac{\hat{p}_x^2}{2m}, -\hat{z}\hat{p}_y \right] + \left[\frac{\hat{p}_y^2}{2m}, -\hat{z}\hat{p}_y \right] + \left[\frac{\hat{p}_z^2}{2m}, -\hat{z}\hat{p}_y \right] \\
&\quad + [V(r), \hat{y}\hat{p}_z] + [V(r), -\hat{z}\hat{p}_y] \\
&= \left[\frac{\hat{p}_y^2}{2m}, \hat{y}\hat{p}_z \right] + \left[\frac{\hat{p}_z^2}{2m}, -\hat{z}\hat{p}_y \right] + i\hbar \left(\hat{y}\frac{\partial V}{\partial z} - \hat{z}\frac{\partial V}{\partial y} \right) \\
&= -\frac{i\hbar\hat{p}_y\hat{p}_z}{m} + \frac{i\hbar\hat{p}_y\hat{p}_z}{m} + i\hbar\frac{\partial V}{\partial r}\left(\hat{y}\frac{\partial r}{\partial z} - \hat{z}\frac{\partial r}{\partial y} \right) \\
&= 0
\end{aligned}$$

  - Now let's investigate some of the above substitutions a bit more closely.
  - From line 1 to line 2, we split the commutator into $4 \cdot 2 = 8$ terms using its bilinearity.

– From line 2 to line 3, we eliminated all commutators that go to zero among the first six, and evaluated the last two commutators using a combination of Rule 3 and properties mentioned at the beginning of the lecture.

■ Notice that the only two of the first six commutators that did *not* go to zero were those for which the variable in the squared momentum operator matched the position operator, i.e., in

$$\left[\frac{\hat{p}_y^2}{2m}, \hat{y}\hat{p}_z\right]$$

we may observe that $\hat{p}_y^2$ and $\hat{y}$ both concern y.

■ Example evaluation:

$$\begin{aligned}
\left[\frac{\hat{p}_x^2}{2m}, \hat{y}\hat{p}_z\right] &= \frac{1}{2m}[\hat{p}_x^2, \hat{y}\hat{p}_z] && \text{Rule 4}\\
&= \frac{1}{2m}(\hat{p}_x[\hat{p}_x, \hat{y}\hat{p}_z] + [\hat{p}_x, \hat{y}\hat{p}_z]\hat{p}_x) && \text{Rule 1}\\
&= \frac{1}{2m}(\hat{p}_x(\hat{y}\underbrace{[\hat{p}_x, \hat{p}_z]}_{0} + \underbrace{[\hat{p}_x, \hat{y}]}_{0}\hat{p}_z) + (\hat{y}\underbrace{[\hat{p}_x, \hat{p}_z]}_{0} + \underbrace{[\hat{p}_x, \hat{y}]}_{0}\hat{p}_z)\hat{p}_x) && \text{Rule 3}\\
&= 0
\end{aligned}$$

■ Example evaluation:

$$\begin{aligned}
\left[\frac{\hat{p}_y^2}{2m}, \hat{y}\hat{p}_z\right] &= \frac{1}{2m}[\hat{p}_y^2, \hat{y}\hat{p}_z] && \text{Rule 4}\\
&= \frac{1}{2m}(\hat{p}_y[\hat{p}_y, \hat{y}\hat{p}_z] + [\hat{p}_y, \hat{y}\hat{p}_z]\hat{p}_y) && \text{Rule 1}\\
&= \frac{1}{2m}(\hat{p}_y(\hat{y}\underbrace{[\hat{p}_y, \hat{p}_z]}_{0} + \underbrace{[\hat{p}_y, \hat{y}]}_{-i\hbar}\hat{p}_z) + (\hat{y}\underbrace{[\hat{p}_y, \hat{p}_z]}_{0} + \underbrace{[\hat{p}_y, \hat{y}]}_{-i\hbar}\hat{p}_z)\hat{p}_y) && \text{Rule 3}\\
&= \frac{1}{2m}(\hat{p}_y(-i\hbar\hat{p}_z) + (-i\hbar\hat{p}_z)\hat{p}_y)\\
&= -\frac{i\hbar}{2m}(\hat{p}_y\hat{p}_z + \hat{p}_z\hat{p}_y)\\
&= -\frac{i\hbar}{2m}(\hat{p}_y\hat{p}_z + \hat{p}_y\hat{p}_z)\\
&= -\frac{i\hbar\hat{p}_y\hat{p}_z}{m}
\end{aligned}$$

➢ Note that $\hat{p}_z\hat{p}_y = \hat{p}_y\hat{p}_z$ because $[\hat{p}_y, \hat{p}_z] = 0$.

■ Example evaluation:

$$\begin{aligned}
[V(r), \hat{y}\hat{p}_z] &= \hat{y}\underbrace{[V(r), \hat{p}_z]}_{i\hbar\,\partial V/\partial z} + \underbrace{[V(r), \hat{y}]}_{0}\hat{p}_z && \text{Rule 3}\\
&= i\hbar\hat{y}\frac{\partial V}{\partial z}
\end{aligned}$$

– From line 3 to line 4, we evaluated the last two commutators and applied the chain rule.

– From line 4 to line 5, we algebraically expanded and cancelled everything (using $r = \sqrt{x^2 + y^2 + z^2}$ for the partial derivatives).

– Moving on, similar to the above, we obtain that

$$[\hat{H}, \hat{L}_y] = [\hat{H}, \hat{L}_z] = 0$$

  - Thus, by bilinearity once more,

$$[\hat{H}, \hat{\vec{L}}] = [\hat{H}, \hat{L}_x + \hat{L}_y + \hat{L}_z] = 0$$

- Task 2: The fact that the Hamiltonian commutes with the constant $\hat{\vec{L}}^{\,2}$ is obvious, implying the claim.
- Task 3.
  - Here, we want to investigate if

$$[\hat{L}_x, \hat{L}_y] \stackrel{?}{=} 0$$

  - We do this via

$$\begin{aligned}[\hat{L}_x, \hat{L}_y] &= [\hat{y}\hat{p}_z - \hat{z}p_y, p_x z - x p_z] \\ &= [yp_z, p_x z] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] \\ &= \hat{y}\hat{p}_x(-i\hbar) + \hat{p}_y\hat{x}(i\hbar) \\ &= i\hbar\hat{L}_z\end{aligned}$$

  - Similarly, we can see that no $\hat{L}_i$'s commute with each other. Indeed, altogether, we have

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z \qquad [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x \qquad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$$

- Task 4.
  - We have that

$$\begin{aligned}[\hat{\vec{L}}^{\,2}, \hat{L}_x] &= [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_x] \\ &= 0 + [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x] \\ &= \hat{L}_y[\hat{L}_y, \hat{L}_x] + [\hat{L}_y, \hat{L}_x]\hat{L}_y + \hat{L}_z[\hat{L}_z, \hat{L}_x] + [\hat{L}_z, \hat{L}_x]\hat{L}_z \\ &= \hat{L}_y(-i\hbar\hat{L}_z) + (-i\hbar\hat{L}_z)\hat{L}_y + \hat{L}_z(i\hbar\hat{L}_y) + (i\hbar\hat{L}_y)\hat{L}_z \\ &= i\hbar(-\hat{L}_y\hat{L}_z - \hat{L}_z\hat{L}_y + \hat{L}_z\hat{L}_y + \hat{L}_y\hat{L}_z) \\ &= 0\end{aligned}$$

  - Thus, the squares commute:

$$[\hat{\vec{L}}^{\,2}, \hat{L}_x] = [\hat{\vec{L}}^{\,2}, \hat{L}_y] = [\hat{\vec{L}}^{\,2}, \hat{L}_z] = 0$$

- Conclusion.
  - $\hat{L}_i, \hat{\vec{L}}^{\,2}$ are conserved. That is,

$$[\hat{H}, \hat{L}_i] = [\hat{H}, \hat{\vec{L}}^{\,2}] = 0$$

    - This means that $\hat{H}, \hat{L}_z, \hat{\vec{L}}^{\,2}$ have compatible observables.
    - In other words, we can only define the angular momentum in one direction and the modulus of the angular momentum squared.
  - All this will characterize three-dimensional motion as we'll see.

5.2 Angular Momentum; Ladder Operators

1/31:

- Is there an operator $\hat{L}$?
  - There *is* an operator $\hat{\vec{L}}$ with components $\hat{L}_x, \hat{L}_y, \hat{L}_z$; it's just that we cannot measure it because the components are incompatible.
  - This is why we measure $\hat{\vec{L}}^2$ and one $\hat{L}_i$.
- Recap of 3D.
  - The 3D Hamiltonian is
$$\hat{H} = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r})$$
  - We are interested in obtaining the energy eigenvalues of such a potential, which we do via the 3D Schrödinger equation,
$$\hat{H}\psi(\vec{r}, t) = E\psi(\vec{r}, t)$$
  - The potentials we work with will be **central**, i.e.,
$$V(\vec{r}) = V(r)$$
  - For central potentials, we have the following compatibility relations.
$$[\hat{H}, \hat{L}_z] = [\hat{H}, \hat{L}_x] = [\hat{H}, \hat{L}_y] = [\hat{H}, \hat{\vec{L}}^2] = [\hat{\vec{L}}^2, \hat{L}_z] = 0$$
$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$$
  - Thus, we can get good eigenstates of $\hat{H}$, $\hat{\vec{L}}^2$, and $\hat{L}_z$ all together.
    - We choose $\hat{L}_z$ instead of $\hat{L}_x, \hat{L}_y$ WLOG.
- **Central** (potential): A potential that depends only on the distance.
- Before we go any further, we need to express the Laplacian
$$\vec{\nabla}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$
in spherical coordinates.
  - Recall that spherical coordinates have a distance r, a polar angle θ, and an azimuthal angle ϕ.
  - Drawing out the Cartesian and polar coordinates of a point, we may rederive that
$$z = r\cos\theta$$
$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
  - The Laplacian has a rather nasty form in spherical coordinates. In particular, it is given by
$$\vec{\nabla}^2\psi(r, \theta, \phi) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}$$
- A nice thing about spherical coordinates is that like $\hat{p}_z = -i\hbar\,\partial/\partial z$ in Cartesian coordinates, we have in spherical coordinates that
$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

- Eigenstates of $\hat{L}_z$.
  - We wish to solve
    $$\hat{L}_z\psi = c\psi$$
    where ψ is the desired eigenstate and c the corresponding eigenvalue.
  - Expanding, we have that
    $$\begin{aligned} -i\hbar\frac{\partial\psi}{\partial\phi} &= c\psi \\ \frac{\partial\psi}{\partial\phi} &= \frac{ic}{\hbar}\psi \\ \psi(r,\theta,\phi) &= F(r,\theta)\mathrm{e}^{ic\phi/\hbar} \end{aligned}$$
  - We now apply the boundary condition to determine c. Since
    $$\begin{aligned} \psi(r,\theta,\phi+2\pi) &= \psi(r,\theta,\phi) \\ \mathrm{e}^{2\pi ic/\hbar} &= 1 \end{aligned}$$
    we must have that $c/\hbar = m \in \mathbb{Z}$.
  - Thus, ψ as written above is an eigenstate of $\hat{L}_z$ with eigenvalue $\hbar m$.
  - Sanity check:
    $$\hat{L}_z\psi = -i\hbar(im)F(r,\theta)\mathrm{e}^{im\phi} = \hbar m\psi$$
- **Ladder operator**: Either of the two operators defined as follows. *Denoted by* $\hat{\boldsymbol{L}}_{\boldsymbol{\pm}}$. *Given by*
  $$\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y$$
- Commutator of the ladder operators and the angular momentum operators.
  - We have by the the commutator relations among the $\hat{L}_i$ that
    $$[\hat{L}_\pm, \hat{L}_z] = [\hat{L}_x \pm i\hat{L}_y, \hat{L}_z] = -i\hbar\hat{L}_y \pm i(i\hbar\hat{L}_x) = -i\hbar\hat{L}_y \mp \hbar\hat{L}_x = \mp\hbar(\hat{L}_x \pm i\hat{L}_y) = \mp\hbar\hat{L}_\pm$$
- Commutator of the ladder operators with each other.
  - We have that
    $$\begin{aligned} \hat{L}_+\hat{L}_- &= (\hat{L}_x + i\hat{L}_y)(\hat{L}_x - i\hat{L}_y) \\ &= \hat{L}_x^2 + \hat{L}_y^2 + i(\hat{L}_y\hat{L}_x) - i(\hat{L}_x\hat{L}_y) \\ &= \hat{L}_x^2 + \hat{L}_y^2 - i[\hat{L}_x, \hat{L}_y] \\ &= \hat{L}_x^2 + \hat{L}_y^2 + \hbar\hat{L}_z \\ &= \hat{L}_x^2 + \hat{L}_y^2 + \hbar\hat{L}_z + \hat{L}_z^2 - \hat{L}_z^2 \\ &= \hat{\vec{L}}^{\,2} - \hat{L}_z^2 + \hbar\hat{L}_z \end{aligned}$$
  - Similarly, we have that
    $$\begin{aligned} \hat{L}_-\hat{L}_+ &= (\hat{L}_x - i\hat{L}_y)(\hat{L}_x + i\hat{L}_y) \\ &= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 - i[\hat{L}_y, \hat{L}_x] - \hat{L}_z^2 \\ &= \hat{\vec{L}}^{\,2} - \hat{L}_z^2 - \hbar\hat{L}_z \end{aligned}$$
  - Thus, we can calculate that
    $$[\hat{L}_+, \hat{L}_-] = 2\hbar\hat{L}_z$$

- The ladder operators also "raise" and "lower."
  - Let $|\ell, m\rangle$ be an eigenstate of $\hat{\vec{L}}^2, \hat{L}_z$.
  - Then we have the following, where we will withhold proof of the left equality below for now.

$$\hat{\vec{L}}^2 |\ell, m\rangle = \hbar^2 \ell(\ell+1) |\ell, m\rangle \qquad \hat{L}_z |\ell, m\rangle = \hbar m |\ell, m\rangle$$

  - Now, what happens when we apply $\hat{L}_z$ to $\hat{L}_+ |\ell, m\rangle$? As we might expect at this point,

$$\begin{aligned} \hat{L}_z(\hat{L}_+ |\ell, m\rangle) &= \left[\hat{L}_+\hat{L}_z - (\hat{L}_+\hat{L}_z - \hat{L}_z\hat{L}_+)\right] |\ell, m\rangle \\ &= \hat{L}_+ \hbar m |\ell, m\rangle + \hbar \hat{L}_+ |\ell, m\rangle \\ &= \hbar(m+1)(\hat{L}_+ |\ell, m\rangle) \end{aligned}$$

  - Thus,

$$\hat{L}_+ |\ell, m\rangle \propto |\ell, m+1\rangle$$

  - We can prove in a similar fashion that

$$\hat{L}_- |\ell, m\rangle \propto |\ell, m-1\rangle$$

- Relating the numbers m, ℓ.
  - Recall that $\hat{\vec{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$.
  - The eigenvalue corresponding to an eigenstate of $\hat{\vec{L}}^2$ is $\hbar^2\ell(\ell+1)$.
  - The eigenvalue corresponding to an eigenstate of $\hat{L}_z^2$ is $(\hbar m)^2$.
  - Thus, since all quantities are positive, $\hbar^2\ell(\ell+1) > \hbar^2 m^2$; it follows that $|m| < |\ell|$.
  - But since ladder operators give larger and larger values of m without changing ℓ, it appears that eventually, this rule will be violated. Therefore, there must be an $m_{\max}$ such that

$$L_+ |\ell, m_{\max}\rangle = 0$$

  - Similarly, there must be an $m_{\min}$ such that

$$L_- |\ell, m_{\min}\rangle = 0$$

  - Since we have $\hat{\vec{L}}^2 = \hat{L}_-\hat{L}_+ + \hbar\hat{L}_z + \hat{L}_z^2$, we have that

$$\hat{\vec{L}}^2 |\ell, m_{\max}\rangle = \hat{L}_- \underbrace{\hat{L}_+ |\ell, m_{\max}\rangle}_{0} + (\hbar^2 m_{\max} + \hbar^2 m_{\max}^2) |\ell, m_{\max}\rangle$$

  - This combined with the fact that

$$\hat{\vec{L}}^2 |\ell, m_{\max}\rangle = \hbar^2\ell(\ell+1) |\ell, m_{\max}\rangle$$

    implies that

$$m_{\max} = \ell \qquad m_{\min} = -\ell$$

  - Thus, $|\ell, m\rangle$ has $2m+1$ eigenstates for $-\ell \leq m \leq \ell$. Additionally, we have that

$$\hat{\vec{L}}^2 |\ell, m\rangle = \hbar^2\ell(\ell+1) |\ell, m\rangle \qquad \hat{L}_z |\ell, m\rangle = \hbar m |\ell, m\rangle$$

5.3 Spherical Harmonics

2/2:

- Ask Wagner in OH: Did I miss something here, especially as pertains to the spherical harmonic oscillator?? Did you cover something not in the lecture notes?
- Recall our discussion of spherical coordinates from last time, where we derived

$$\vec{\nabla}^2\psi(r,\theta,\phi) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}$$

- Once we've defined the Laplacian in spherical coordinates, we can obtain the energy eigenvalues as per usual via

$$\left[-\frac{\hbar^2}{2M}\vec{\nabla}^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}) \qquad \psi(\vec{r},t) = \psi(\vec{r})\mathrm{e}^{-iEt/\hbar}$$

- Now observe that $\vec{\nabla}^2$ has a clear separation of a radial differential operator and an angular one (i.e., the left term is added to the two right ones). Hence, we shall consider a solution

$$\psi(\vec{r}) = R(r)Y(\theta,\phi)$$

- Thus,

$$-\frac{\hbar^2}{2M}\left[\frac{Y}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] + [V(r)-E]RY = 0$$

- Now divide the above by $R(r)\cdot Y(\theta,\phi)$.

$$-\frac{\hbar^2}{2M}\frac{1}{R}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + V(r) - E - \frac{\hbar^2}{2M}\left[\frac{1}{Y}\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{Y}\frac{1}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = 0$$

- Multiplying by $2Mr^2/\hbar^2$ yields an expression that is a sum of a function of only r with a function of only θ,ϕ. Hence, for them to vanish, they should be equal to the same constant, which we will write in a strange way to be justified later.

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} = -\ell(\ell+1)Y$$
$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2Mr^2}{\hbar^2}[V(r)-E] = \ell(\ell+1)R$$

Week 6

Central Potentials & Midterm

6.1 Central Potentials

2/5:

- Review.
  - Definition of **central potential**.
    - In this case, we have three good observables: $\hat{H}, \hat{\vec{L}}^2, \hat{L}_z$.
  - Last Friday, we discovered that the eigenstates are characterized by three numbers n, ℓ, m that correspond to the three operators above.
    - Altogether, we have that

$$\hat{L}_z |n\ell m\rangle = \hbar m |n\ell m\rangle \qquad \hat{\vec{L}}^2 |n\ell m\rangle = \hbar^2 \ell(\ell+1) |n\ell m\rangle \qquad \hat{H} |n\ell m\rangle = E_n |n\ell m\rangle$$

  - We also defined ladder operators L_+, L_- such that

$$\hat{L}_\pm |n\ell m\rangle = \sqrt{\ell(\ell+1) - m(m\pm 1)} |n\ell(m\pm 1)\rangle$$

- **Central potential**: A three-dimensional potential energy distribution in which the potential depends only on the distance from the origin. *Denoted by* $\boldsymbol{V(r)}$.
- The eigenstates are well normalized, i.e.,

$$\langle n\ell m | n\ell m' \rangle = \delta_{mm'}$$

  - It follows that

$$\langle n\ell m | \hat{L}_x | n\ell m \rangle = \langle n\ell m | \frac{1}{2}(\hat{L}_+ + \hat{L}_-) | n\ell m \rangle = 0$$

  - Similarly,

$$\langle n\ell m | \hat{L}_y | n\ell m \rangle = 0$$

  - Additionally, we have that

$$\langle n\ell m | (\hat{L}_x^2 + \hat{L}_y^2) | n\ell m \rangle = \langle n\ell m | (\hat{\vec{L}}^2 - \hat{L}_z^2) | n\ell m \rangle = \hbar^2[\ell(\ell+1) - m^2]$$

    - Since the above eigenvalue must be greater than or equal to zero, $|m| \leq \ell$.
  - Recall that $\hat{L}_x, \hat{L}_y$ are incompatible with $\hat{L}_z$.
    - This is why we have an uncertainty associated with the quantity $\hbar^2[\ell(\ell+1) - m^2]$.
    - This is also why we have

$$\langle n\ell m | (\hat{L}_x^2 + \hat{L}_y^2) | n\ell m \rangle = 2 \langle n\ell m | \hat{L}_x^2 | n\ell m \rangle = 2 \langle n\ell m | \hat{L}_y^2 | n\ell m \rangle$$

- Recall expressing the wave function in polar coordinates via $\psi(r,\theta,\phi)$.
  - Solving by separation of variables, we have
$$|n\ell m\rangle = \psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)\cdot Y_{\ell m}(\theta,\phi)$$
  - This has the interesting property that if we define
$$U_{n\ell}(r) = rR_{n\ell}(r)$$
then
$$-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2}{\mathrm{d}r^2}[U_{n\ell}(r)] + \underbrace{\left[\frac{\hbar^2\ell(\ell+1)}{2Mr^2} + V(r)\right]}_{V_{\text{eff}}(r)} U_{n\ell}(r) = E_{n\ell}U_{n\ell}(r)$$
  - This means that U is the solution to a one-dimensional problem in an effective potential.
- A couple of interesting comments.
  - m doesn't appear because directionality doesn't matter. We don't care which direction we project into; we only care about the total angular momentum.
    - Recall that there is a $2\ell+1$ degeneracy associated with the fact that m doesn't appear.
    - Indeed, we get energy levels within this potential.
  - Recall that M denotes the mass to avoid confusion with the quantum number m.
  - The effective potential we are considering is of the same shape as the red line in Figure 5.1.
- Recall that solving for Y, we obtain
$$\underbrace{-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y_{\ell m}}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y_{\ell m}}{\partial\phi^2}\right]}_{\hat{\vec{L}}^{\,2}Y_{\ell m}} = \hbar^2\ell(\ell+1)Y_{\ell m}$$
  - The rather complicated expression on the left above just describes $\hat{\vec{L}}^{\,2}Y_{\ell m}$ in polar coordinates.
  - We'll get as a solution
$$Y_{\ell m}(\theta,\phi) = \mathrm{e}^{im\phi}\Theta_{\ell m}(\theta)$$
  - We can therefore see that if $\hat{L}_z = -i\hbar(\,\partial/\partial\phi\,)$ then
$$\hat{L}_z Y_{\ell m}(\theta,\phi) = \hbar m Y_{\ell m}(\theta,\phi)$$
  - Remember that m and ℓ are both integers.
  - Simplifying the above, we get
$$\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta_{\ell m}}{\mathrm{d}\theta}\right) - m^2\Theta_{\ell m} + [\ell(\ell+1)\sin^2\theta]\Theta_{\ell m} = 0$$
  - Secretly, all the dependence on θ is a dependence on $\cos\theta$ since we can make substitutions like $\sin^2\theta = 1-\cos^2\theta$.
  - The solutions are then
$$\Theta_{\ell m}(u) = AP_\ell^m(u)$$
where $u=\cos\theta$ and P_ℓ^m are the **associated Legendre functions**.
  - Finally, if we want to obtain a well-normalized solution, i.e., we need to calculate A. Computationally, this means that we need
$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\mathrm{d}r\,\mathrm{d}\theta\mathrm{d}\phi\; r^2\sin\theta|Y_{\ell m}(\theta,\phi)R_{n\ell}(r)|^2$$

– This integral splits into two.

$$\int_0^{2\pi}\int_0^{\pi} \mathrm{d}\theta\mathrm{d}\phi\ \sin\theta|Y_{\ell m}(\theta,\phi)|^2 = 1 \qquad \int_0^{\infty} \mathrm{d}r\ \underbrace{|rR_{n\ell}(r)|^2}_{|U_{n\ell}(r)|^2} = 1$$

– Note that this implies that

$$\int \mathrm{d}\phi\mathrm{d}\theta\ \sin\theta Y_{\ell m}(\theta,\phi)Y_{\ell' m'}(\theta,\phi) = \delta_{\ell\ell'}\delta_{mm'} \qquad \int \mathrm{d}r\ r^2 R_{n\ell}(r)R_{n'\ell'}(r) = \delta_{nn'}\delta_{\ell\ell'}$$

- **Rodrigues formula**: The formula given as follows. *Given by*

$$\frac{1}{2^\ell \ell!}\frac{\mathrm{d}^\ell}{\mathrm{d}u^\ell}\left(u^2-1\right)^\ell$$

- **Legendre polynomials**: The system of complete orthogonal polynomials defined via the Rodrigues formula. *Denoted by* $\boldsymbol{P_\ell(u)}$. *Given by*

$$P_\ell(u) = \frac{1}{2^\ell \ell!}\frac{\mathrm{d}^\ell}{\mathrm{d}u^\ell}\left(u^2-1\right)^\ell$$

- **Associated Legendre functions**: The canonical solutions of the general Legendre equation. *Denoted by* $\boldsymbol{P_\ell^m(u)}$. *Given by*

$$P_\ell^m(u) = (1-u^2)^{|m|/2}\frac{\mathrm{d}^{|m|}}{\mathrm{d}u^{|m|}}[P_\ell(u)]$$

- A couple of closing comments.

– The normalization constant is such that *en toto*,

$$Y_{\ell m}(\theta,\phi) = (-1)^m\sqrt{\frac{(2\ell+1)}{4\pi}\cdot\frac{(\ell-m)!}{(\ell+m)!}}P_{\ell m}(\cos\theta)\mathrm{e}^{im\phi}$$

■ This is for $m \geq 0$

– If $m < 0$, then use

$$Y_{\ell(-|m|)} = (-1)^{|m|}Y^*_{\ell|m|}(\theta,\phi)$$

where the complex conjugate of Y just switches the exponential term at the end to $\mathrm{e}^{-im\phi}$.

– The probability $P_{00}(\cos\theta)$ is a constant. So if we draw a circle in the zx-plane, it will not vary in intensity??

– We also have $P_{10}(\cos\theta) = \cos\theta$. Thus, this particle will move more quickly past the x-axis and slower toward the bottom of its circular orbit, yielding a p-orbital shape. Maximum probability is moving in the perpendicular direction.

– $P_{11}(\cos\theta) = \sin\theta$.

■ If you have a particle with angular momentum 1 and modulus 1, it moves in the xy plane in such a way that the total angular momentum points in the vertical direction and thus then it has maximum probability of being in the perpendicular plane.

■ This gives us something sideways (think p_z vs. p_x orbitals).

6.2 Midterm Exam Review

2/7:

- Format of the midterm.
  - 5 conceptual questions (multiple choice) that we should know by now.
  - Two computational problems.
    - One that appears in the problem set.
    - One that appears in the problem set but we will have to do a couple extra things.
    - Subject: One on harmonic oscillators and one on motion in potential wells.
  - If we fail the multiple choice, "something is wrong with you."
  - The exam is not curved, but the class will have a curve.
  - We can bring virtual notes.
- Conceptual things to remember for the midterm.
  - In classical mechanics, a particle is given by a path/trajectory $\vec{r}(t)$.
  - In quantum mechanics, there is no path. The best we can do is define $\langle\psi|\vec{r}|\psi\rangle(t)$, but we will always be hampered by the fact that $\sigma_{\vec{p}} \neq 0$.
    - The uncertainty in momentum comes from the Heisenberg uncertainty relation.
    - If the operator is independent of time (such as $\hat{x}, \hat{p}_x, \hat{\vec{r}}, \hat{\vec{p}}, V(\vec{r})$), then
    $$\frac{\mathrm{d}}{\mathrm{d}t}\Big(\langle\psi|\hat{O}|\psi\rangle\Big) = \frac{i}{\hbar}\langle\psi|[\hat{H},\hat{O}]|\psi\rangle$$
      - ➢ This means that if $[\hat{H},\hat{O}] = 0$, then the expected value of the operator is independent of time.
    - We most often deal with time-independent potentials $V(\vec{r},t) = V(\vec{r})$.
    - Recall that since $[\hat{H},\hat{H}] = 0$, $E = \langle\psi|\hat{H}|\psi\rangle$ is a good quantum number.
      - ➢ It follows that
      $$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle \qquad\qquad \hat{H}^2|\psi_n\rangle = E_n^2|\psi_n\rangle$$
      - ➢ We also have that
      $$\sigma_{\hat{H}} = 0 \qquad\qquad \langle\psi_n|\hat{H}^2|\psi_n\rangle - (\langle\psi_n|\hat{H}|\psi_n\rangle)^2 = 0$$
    - It is very important to remember that
    $$\begin{aligned}|\psi\rangle &= \sum_n c_n \mathrm{e}^{-iE_nt/\hbar}|\psi_n\rangle\\ \langle\psi|\psi\rangle &= \sum_n |c_n|^2 = 1\\ \langle\psi|\hat{H}|\psi\rangle &= \sum_n |c_n|^2 E_n\\ \langle\psi_n|\psi_m\rangle &= \int \mathrm{d}\vec{r}\ \psi_n^*\psi_m = \delta_{nm}\end{aligned}$$
      - ➢ It follows from the bottom three statements that $|c_n|^2$ is the probability of measuring E_n.
    - We can obtain the m^{th} coefficient of ψ using the inner product formula.
    $$\langle\psi_m|\psi\rangle = \sum_n c_n \underbrace{\langle\psi_m|\psi_n\rangle}_{\delta_{nm}} = c_m$$
      - ➢ Equivalently,
      $$c_m = \int \mathrm{d}\vec{r}\ \psi_m^*(\vec{r})\psi(\vec{r})$$

- Computational things to remember for the midterm.
- The harmonic oscillator.
  - Since we are in one dimension, $\hat{p} = \hat{p}_x$
  - The Hamiltonian is
$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{k\hat{x}^2}{2}$$
  - We have that
$$[\hat{p}, \hat{x}] = -i\hbar$$
    - Note that this statement is not only true in the context of the harmonic oscillator. Indeed, $\hat{p}_x$ and $\hat{x}$ always compatibilize in this way.
  - Recall that compatibility is important because the *generic* uncertainty principle (restated as follows) requires a zero commutator in order for it to be possible for both uncertainties to be zero!
$$\sigma_{\hat{A}}^2 \sigma_{\hat{B}}^2 \geq \frac{1}{4} |\langle\psi|[\hat{A}, \hat{B}]|\psi\rangle|^2$$
  - We defined ladder operators
$$a_+ = \frac{1}{\sqrt{2\hbar m\omega}}(-i\hat{p} + m\omega\hat{x}) \qquad a_- = \frac{1}{\sqrt{2\hbar m\omega}}(i\hat{p} + m\omega\hat{x})$$
  - Having defined these operators, we may write the Hamiltonian in terms of them as follows.
$$\hat{H} = \hbar\omega\left(a_+a_- + \frac{1}{2}\right)$$
  - Defining $|n\rangle := |\psi_n\rangle$ and remembering that
$$a_+a_- |n\rangle = n|n\rangle$$
    this form of the Hamiltonian makes it obvious that
$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$
    since
$$\hat{H}|n\rangle = \hbar\omega\left(n + \frac{1}{2}\right)|n\rangle \qquad \langle n|\hat{H}|n\rangle = \hbar\omega\left(n + \frac{1}{2}\right)$$
  - The ladder operators also have distinctive actions on the energy eigenstates.
$$a_-|n\rangle = \sqrt{n}\,|n-1\rangle \qquad a_+|n\rangle = \sqrt{n+1}\,|n+1\rangle$$
  - Don't forget that overall,
$$\langle n|m\rangle = \delta_{nm}$$
  - The ladder operators enable us to calculate the observables of a generic state ψ of the harmonic oscillator as follows.
$$\begin{aligned}\langle\psi|\hat{x}|\psi\rangle &= \sqrt{\frac{\hbar}{2M\omega}}\,\langle\psi|(a_+ + a_-)|\psi\rangle \\ &= \sum_{m,n} c_m^* c_n \sqrt{\frac{\hbar}{2M\omega}}\,\langle m|(a_+ + a_-)|n\rangle\, e^{i(E_m - E_n)t/\hbar}\end{aligned}$$

$$= \sum_{m,n} c_m^* c_n \sqrt{\frac{\hbar}{2M\omega}} \mathrm{e}^{i(E_m - E_n)t/\hbar} \left(\sqrt{n+1} \underbrace{\langle m|n+1\rangle}_{\delta_{m,n+1}} + \underbrace{\sqrt{n} \langle m|n-1\rangle}_{\delta_{m,n-1}} \right)$$

$$= \sum_{n=0}^{\infty} c_{n+1}^* c_n \mathrm{e}^{i\omega t} \sqrt{n+1} + \sum_{n=0}^{\infty} c_{n-1}^* c_n \mathrm{e}^{-i\omega t} \sqrt{n}$$

$$= \sum_{n=0}^{\infty} \left(c_{n+1}^* c_n \mathrm{e}^{i\omega t} + c_n^* c_{n+1} \mathrm{e}^{-i\omega t} \right) \sqrt{n+1}$$

- Note that in the next to last line above, the second sum *can* go from zero to ∞ because for the $n = 0$ term, although we have an undefined c_{-1}, we also have $\sqrt{0} = 0$ so the problematic "undefined" term vanishes.
- We can expect to see a computation like this in the midterm.

– Using similar methods, we can calculate that

$$\left\langle n \left| \frac{k\hat{x}^2}{2} \right| n \right\rangle = \frac{E_n}{2} = \langle n|\hat{p}^2|n\rangle = \frac{\hbar\omega}{2} \left(n + \frac{1}{2} \right)$$

- In particular, we expand

$$\langle n|(a_+ + a_-)^2|n\rangle = \underbrace{\langle n|a_+^2|n\rangle}_{0} + \underbrace{\langle n|a_-^2|n\rangle}_{0} + \underbrace{\langle n|a_+a_-|n\rangle}_{n} + \langle n| \underbrace{a_-a_+}_{a_+a_-+1} |n\rangle = 2n+1$$

– Note that for the same reason discussed above,

$$a_-a_+ |n\rangle = (n+1)|n\rangle$$

– Since $\sigma_x^2 = \langle n|\hat{x}^2|n\rangle - (\langle n|\hat{x}|n\rangle)^2 \neq 0$ as we can verify by further calculations, there is *always* some nonzero σ_x for the harmonic oscillator.

• Final note.

– If we want to compute $\langle\psi|\hat{x}|\psi\rangle$ for a generic potential, we must use

$$\langle\psi|\hat{x}|\psi\rangle(t) = \sum_{m,n} c_m^* c_n \mathrm{e}^{i(E_m - E_n)t/\hbar} \langle m|\hat{x}|n\rangle$$

– In other words, it is only in the harmonic oscillator specifically that we can use the ladder operators.

– If we are in a specific energy eigenstate (of a general potential), though, then we do get conservation of position and momentum because $E_m = E_n$ so $E_m - E_n = 0$ removes the time term. In particular,

$$\langle\psi_n(x,t)|\hat{x}|\psi_n(x,t)\rangle = c_n^* c_n \mathrm{e}^{i(E_n - E_n)t/\hbar} \langle\psi_n(x)|\hat{x}|\psi_n(x)\rangle = c_n^* c_n \langle\psi_n(x)|\hat{x}|\psi_n(x)\rangle$$

and

$$\frac{\mathrm{d}}{\mathrm{d}t}(\langle\psi_n|\hat{x}|\psi_n\rangle) = \frac{i}{\hbar}\langle\psi_n|[\hat{H},\hat{x}]|\psi_n\rangle = \frac{i}{\hbar}\langle\psi_n|\hat{H}\hat{x} - \hat{x}\hat{H}|\psi_n\rangle = \frac{i}{\hbar}(E_n\langle\psi_n|\hat{x}|\psi_n\rangle - E_n\langle\psi_n|\hat{x}|\psi_n\rangle) = 0$$

so

$$\frac{\mathrm{d}}{\mathrm{d}t}(\langle\psi_n|\hat{x}|\psi_n\rangle) = \frac{\mathrm{d}}{\mathrm{d}t}(\langle\psi_n|\hat{p}|\psi_n\rangle) = 0$$

- Why does $\langle\psi_n|\hat{H}\hat{x}|\psi_n\rangle = E_n\langle\psi_n|\hat{x}|\psi_n\rangle$?? I thought $\hat{H}$ and $\hat{x}$ didn't commute.

6.3 Midterm

2/9:

1. (5 pts) In quantum mechanics, a particle follows a definite path $\vec{r} = \vec{r}(t)$. The only difference with the classical case is that the energy is quantized.

- **a.** True
- **b.** False

2. (5 pts) A particle can enter a region of space where the energy of the particle is smaller than the potential energy.

- **a.** False
- **b.** True, if it happens in a limited region of space.

3. (5 pts) In quantum mechanics, observables are identified with Hermitian operators. These observables are conserved in time...

- **a.** Only if these operators commute with the momentum operator;
- **b.** Only if these operators commute with the Hamiltonian operator;
- **c.** Only if these operators commute with the Hamiltonian operator and they have no explicit time dependence.

Give a short justification of your answer.

4. (5 pts) For the case of a time-independent potential, one can find eigenfunctions of the Hamiltonian operator $\psi_n(x)$ in which the energy E_n is well-defined. Being that the case, the mean values of the position and momentum in the states described by $\psi_n(x,t) = \psi_n(x)\mathrm{e}^{-iE_nt/\hbar}$ are independent of time.

- **a.** True
- **b.** False

Give a short justification of your answer.

5. Given the eigenfunctions $\psi_n(x)$ of the Hamiltonian in one dimension with well-defined energies E_n...

- **a.** (5 pts) Write the form of the general solution $\psi(x,t)$, including its time dependence.
- **b.** (5 pts) What is the mean value of the Hamiltonian in the state associated with this general solution, and how can this expression be interpreted in terms of the probability of measuring the particle with a given energy E_n?
- **c.** (10 pts) Write the formal expression one needs to calculate to obtain the mean values of the position and momentum, identified with the operators $\hat{x}$ and $\hat{p}_x = -i\hbar(\partial/\partial x)$ in terms of the coefficients c_n, $\psi_n(x)$, E_n, x, and the derivatives with respect to x of ψ_n. Include the dependence on time.

6. For the harmonic oscillator, consider the ladder operators $a_\pm = (\mp i\hat{p} + M\omega x)/\sqrt{2\hbar M\omega}$ such that $[a_-, a_+] = 1$, where M is the mass of the particle. The Hamiltonian may be written as $\hat{H} = \hbar\omega(a_+a_- + 1/2)$, and the eigenstates of energy $E_n = \hbar\omega(n + 1/2)$ are related by $a_+\psi_n = \sqrt{n+1}\psi_{n+1}$, $a_-\psi_n = \sqrt{n}\psi_{n-1}$. Some additional useful formulae are given after Problem 7.

- **a.** (5 pts) Compute the mean value of $\hat{x}$ and $\hat{p}$ in the energy eigenstates described by ψ_n.
- **b.** (10 pts) Compute the mean value of $\hat{x}^2$ and $\hat{p}^2$ in these states.
- **c.** (5 pts) Verify that the uncertainty principle is fulfilled for the energy eigenstates.
- **d.** (15 pts) Write the expression for the mean value of the momentum for the general solution $\psi(x,t)$. Work it out as much as you can. What can you say about the frequency of oscillation of the momentum in a generic solution?

7. Imagine a particle in an infinite potential well

$$V(x) = \begin{cases} 0 & 0 < x < a \\ \infty & x \leq 0 \text{ and } x \geq a \end{cases}$$

Some useful formulae for the solution of Problem 7 are given below.

a. (10 pts) What are the energy eigenvalues and eigenstate wave functions in this case? Justify your answer.

b. (15 pts) Take a superposition of two energy eigenstates with contiguous eigenvalues

$$\psi(x,t) = \frac{1}{\sqrt{2}}\psi_n(x,t) + \frac{1}{\sqrt{2}}\psi_{n+1}(x,t)$$

anc compute the mean value of $\hat{x}$ as a function of time for the wave function $\psi(x,t)$. Compute also the mean value of the momentum and demonstrate from these expressions that it is related to the mean value of $\hat{x}$ by the expected Ehrenfest Theorem relation:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\,\langle\psi|\hat{x}|\psi\rangle) = \frac{\langle\psi|\hat{p}|\psi\rangle}{M}$$

Some Useful Formulae

For the Harmonic Oscillator

$$\hat{p} = i\sqrt{\frac{\hbar M\omega}{2}}(a_+ - a_-) \qquad\qquad \hat{x} = \sqrt{\frac{\hbar}{2M\omega}}(a_+ + a_-)$$

Matrix elements: Using Dirac notation,

$$\begin{aligned} a_+\,|n\rangle &= \sqrt{n+1}\,|n+1\rangle \\ a_-\,|n\rangle &= \sqrt{n}\,|n-1\rangle \\ \langle n|(a_+)^m|n\rangle &= \langle n|(a_-)^m|n\rangle = 0, \quad m \geq 1 \\ \langle m|a_+|n\rangle &= \sqrt{n+1}\,\delta_{n+1,m} \\ \langle m|a_-|n\rangle &= \sqrt{n}\,\delta_{n-1,m} \\ \langle m|a_-a_+|n\rangle &= (n+1)\delta_{n,m} \\ \langle m|a_+a_-|n\rangle &= n\,\delta_{n,m} \end{aligned}$$

For the Harmonic Oscillator

Wave functions and energies:

$$\psi_n(x,t) = \sqrt{\frac{2}{a}}\sin\Big(\frac{\pi n x}{a}\Big)\mathrm{e}^{-iE_n t/\hbar} \qquad\qquad E_n = \frac{\hbar^2\pi^2 n^2}{2Ma^2}$$

Useful integrals: For $n, m \in \mathbb{N}$,

$$\frac{2}{a}\int_0^a \sin\Big(\frac{\pi n x}{a}\Big)\sin\Big(\frac{\pi m x}{a}\Big)\,\mathrm{d}x = \delta_{nm}$$

$$\frac{2}{a}\int_0^a x\sin^2(\frac{\pi n x}{a})\,\mathrm{d}x = \frac{a}{2}$$

For $n+m$ even and $n \neq m$,

$$\frac{2}{a}\int_0^a x\sin\Big(\frac{\pi n x}{a}\Big)\sin\Big(\frac{\pi m x}{a}\Big)\,\mathrm{d}x = 0$$

For $n+m$ even,

$$\int_0^a \sin\Big(\frac{\pi n x}{a}\Big)\cos\Big(\frac{\pi m x}{a}\Big)\,\mathrm{d}x = 0$$

For $n+m$ odd,

$$\frac{2}{a}\int_0^a x\sin\Big(\frac{\pi n x}{a}\Big)\sin\Big(\frac{\pi m x}{a}\Big)\,\mathrm{d}x = -\frac{8anm}{\pi^2(m^2-n^2)^2}$$

$$\frac{\pi m}{a}\frac{2}{a}\int_0^a \sin\Big(\frac{\pi n x}{a}\Big)\cos\Big(\frac{\pi m x}{a}\Big)\,\mathrm{d}x = \frac{4mn}{a(n^2-m^2)}$$

Week 7

Time-Independent Problems in 3D

7.1 Three-Dimensional Harmonic Oscillator

2/12:

- Last time.
  - We discussed some of the problems we face in 3D.
  - The Hamiltonian is now
$$\hat{H} = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] + V(x,y,z)$$
    - Derivatives in three coordinates.
    - The potential is time-independent.
    - If the potential does not depend on anything more specific (e.g., is not central, for instance), then only $\hat{H}$ is conserved.
  - We solve
$$\hat{H}\psi(x,y,z) = E\psi(x,y,z)$$
    for ψ, E.
  - There are three compatible operators:
$$\hat{H},\ \hat{\vec{L}}^2,\ \hat{L}_z$$
    - The z-angular momentum operator, in particular, has the form
$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$
      which is analogous to the form $\hat{p}_z = -i\hbar(\partial/\partial z)$.
  - The potential is central, i.e.,
$$V(x,y,z) = V(r) = V(\sqrt{x^2+y^2+z^2})$$
    - If the potential is depends on r, we solve the ODE in polar coordinates (r,θ,ϕ).
- There are also many cases when we only have
$$V(x,y,z) = V(\sqrt{x^2+y^2})$$
  - In this case, $\hat{H}, \hat{L}_z, \hat{p}_z$ will all be compatible.
- If the potential depends via
$$V(x,y,z) = V(\sqrt{x^2+y^2}, z)$$
  then we will conserve $\hat{H}, \hat{L}_z$.
  - We will play with this in the problem set.

- Today, we begin with the **asymmetric harmonic oscillator**.
- **Asymmetric harmonic oscillator**: A particle subject to the following three-dimensional potential. *Constraint*

$$V(x,y,z) = \frac{M\omega_1^2 x^2}{2} + \frac{M\omega_2^2 y^2}{2} + \frac{M\omega_3^2 z^2}{2}$$

  - This potential is special in the sense that it allows us to solve by separation of variables.
  - In other words, since we can write the ODE in the form

$$\left[-\frac{\hbar^2}{2M}\frac{\partial^2\psi}{\partial x^2} + \frac{M\omega_1^2 x^2}{2}\psi\right] + \left[-\frac{\hbar^2}{2M}\frac{\partial^2\psi}{\partial y^2} + \frac{M\omega_2^2 y^2}{2}\psi\right] + \left[-\frac{\hbar^2}{2M}\frac{\partial^2\psi}{\partial z^2} + \frac{M\omega_3^2 z^2}{2}\psi\right] = E\psi$$

    we may write

$$\psi(x,y,z) = X(x)Y(y)Z(z)$$

  - This allows us to algebraically manipulate the ODE into the form

$$\frac{1}{X}\left[-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} + \frac{M\omega_1^2 x^2}{2}X\right] + \frac{1}{Y}\left[-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2} + \frac{M\omega_2^2 y^2}{2}Y\right] + \frac{1}{Z}\left[-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2Z}{\mathrm{d}z^2} + \frac{M\omega_3^2 z^2}{2}Z\right] = E$$

    - We switch from partial to total derivatives here because now each function is only a function of one variable (e.g., $X(x)$ depends only on x)!
  - Since the sum of these three independent terms is equal to a constant, each term must equal a constant!
  - Splitting the above equation into three, we obtain

$$\begin{aligned}
-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} + \frac{M\omega_1^2 x^2}{2}X &= E_{n_1}X \\
-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2} + \frac{M\omega_2^2 y^2}{2}Y &= E_{n_2}Y \\
-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2Z}{\mathrm{d}z^2} + \frac{M\omega_3^2 z^2}{2}Z &= E_{n_3}Z
\end{aligned}$$

    - It follows that

$$E = E_{n_1} + E_{n_2} + E_{n_3}$$

  - We already know the solution to each of these three ODEs! They are just quantum harmonic oscillators. Thus,

$$E_{n_i} = \hbar\omega_i\left(n_i + \frac{1}{2}\right)$$

    and

$$E = E_{n_1 n_2 n_3} = \hbar\omega_1\left(n_1 + \frac{1}{2}\right) + \hbar\omega_2\left(n_2 + \frac{1}{2}\right) + \hbar\omega_3\left(n_3 + \frac{1}{2}\right)$$

  - Additionally, it follows that the wave functions of each direction are of the form (for example)

$$X_{n_1}(x) = \left(\frac{M\omega_1}{\hbar\pi}\right)^{1/4}\frac{H_{n_1}(\xi_1)}{\sqrt{2^{n_1}n_1!}}\exp\left[-\frac{\xi_1^2}{2}\right]$$

    where $\xi_1 = x\sqrt{M\omega_1/\hbar}$.
- What happens to $X_{n_1}(x), Y_{n_2}(y)$ in the limiting case that $n_1 \to n_2$, $x \to y$, and $\omega_1 \to \omega_2$?
  - We start approaching something interesting.
  - We need to go a bit further, though.

- Now consider the limiting case where
$$\omega_1 = \omega_2 = \omega_3 = \omega$$
  - Herein, the Hamiltonian becomes
$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2M}\vec{\nabla}^2 + \frac{M\omega^2}{2}(x^2+y^2+z^2) \\ &= -\frac{\hbar^2}{2M}\vec{\nabla}^2 + \frac{M\omega^2 r^2}{2}\end{aligned}$$
  - In this *central potential*, recall that we have
$$\hat{\vec{L}}^{\,2} Y_{\ell m}(\theta,\phi) = \hbar^2 \ell(\ell+1) Y_{\ell m}(\theta,\phi)$$
    and
$$\hat{L}_z Y_{\ell m}(\theta,\phi) = \hbar m Y_{\ell m}(\theta,\phi)$$
    and
$$-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2}{\mathrm{d}r^2}[U_{n\ell}(r)] + \underbrace{\left[V(r) + \frac{\hbar^2\ell(\ell+1)}{2Mr^2}\right]}_{V_{\text{eff}}(r)} U_{n\ell}(r) = E_{n\ell}U_{n\ell}(r)$$
- This leads directly into our discussion of the **spherically symmetric harmonic oscillator**.
- **Spherically symmetric harmonic oscillator**: A particle subject to the following one-dimensional effective potential. *Constraint*
$$V_{\text{eff}}(r) = \frac{M\omega^2 r^2}{2} + \frac{\hbar^2\ell(\ell+1)}{2Mr^2}$$

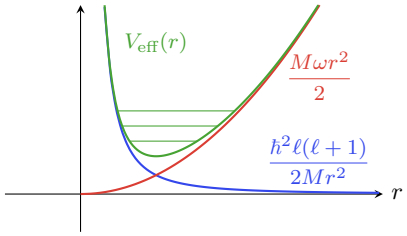


Figure 7.1: Spherically symmetric harmonic oscillator potential.

  - The problem we have to solve here is
$$-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2}{\mathrm{d}r^2}[U_{n\ell}(r)] + \left[\frac{M\omega r^2}{2} + \frac{\hbar^2\ell(\ell+1)}{2Mr^2}\right] U_{n\ell}(r) = E_{n\ell}U(r)$$
  - Recall that
$$\psi(r,\theta,\phi) = R_{n\ell}(r)Y_{\ell m}(\theta,\phi) \qquad\qquad R_{n\ell}(r)r = U_{n\ell}(r)$$
  - In the effective potential, we have the interplay of two peaking potentials as in Figure 7.1.
    - The particle will have certain energy states within the well.
  - In the limiting case that r is small ($r \to 0$), we can approximate the potential as giving us
$$-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2 U_{n\ell}}{\mathrm{d}r^2} + \frac{\hbar^2\ell(\ell+1)}{2Mr^2}U_{n\ell} + \cdots = 0$$

- In this case, the solution is proportional to

$$U_{n\ell} \propto Cr^{\ell+1}$$

- This is because

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(Cr^{\ell+1}\right) = (\ell+1)Cr^{\ell}$$
$$\frac{\mathrm{d}^2}{\mathrm{d}r^2}\left(Cr^{\ell+1}\right) = \ell(\ell+1)C\frac{r^{\ell+1}}{r^2}$$

– In the limiting case that r is large ($r \to \infty$), we can approximate the potential as giving us

$$-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2 U_{n\ell}}{\mathrm{d}r^2} + \frac{M\omega^2 r^2}{2}U_{n\ell} + \cdots = 0$$

- In this case, the solution is proportional to

$$U_{n\ell} = C\mathrm{e}^{-M\omega r^2/2\hbar}$$

– Thus, we combine the two partial solutions to propose the overall ansatz

$$U_{n\ell} = f_{n\ell} r^{\ell+1}\mathrm{e}^{-M\omega r^2/2\hbar}$$

– Substituting back into the original ODE, we obtain the differential equation

$$f''_{n\ell} + 2\left(\frac{\ell+1}{r} - \frac{M\omega r}{\hbar}\right)f'_{n\ell} + \left[\frac{2ME_{n\ell}}{\hbar^2} - \frac{(2\ell+3)M\omega}{\hbar}\right]f_{n\ell} = 0$$

– As we have previously, propose that

$$f_{n\ell}(r) = \sum_j a_j r^j$$

- But there's a problem: $f'_{n\ell}(r=0) = a_1$, and this would allow the $(\ell+1)/r$ term to diverge and make the differential equation blow up.
- Thus, we choose $a_1 = 0$ and proceed.

– Substituting this power series into the differential equation, we obtain

$$\sum_j j(j-1)a_j r^{j-2} + 2\left(\frac{\ell+1}{r} - \frac{M\omega r}{\hbar}\right)\sum_j j a_j r^{j-1} + \left[\frac{2ME_{n\ell}}{\hbar^2} - \frac{(2\ell+3)M\omega}{\hbar}\right]\sum_j a_j r^j = 0$$

– Make a change of variables $j \to j+2$ so that we can start the sum from zero.

$$\sum_{j=0}^{\infty}(j+2)(j+1)a_{j+2}r^j + 2\left(\frac{\ell+1}{r} - \frac{M\omega r}{\hbar}\right)\sum_{j=0}^{\infty}(j+2)a_{j+2}r^{j+1} + \left[\frac{2ME_{n\ell}}{\hbar^2} - \frac{(2\ell+3)M\omega}{\hbar}\right]\sum_{j=0}^{\infty}a_j r^j = 0$$

– We will finish this derivation on Wednesday.

7.2 Office Hours (Yunjia)

2/13:

- PSet 2, Q2c.
  - If we can get up to Equation 12 in the answer key, that's full credit.
  - The thing with κ_{II}^{-1} is the idea that if we have a value that's very large (like κ_{II} will be as $V_0 \to \infty$ since $\kappa_{II} \propto V_0^{1/2}$), then we can Taylor expand in its reciprocal.
    - We cannot Taylor expand in the large values; we can only Taylor expand in small values.
    - This technique is called **perturbation theory** and will be a major topic of QMechII; Yunjia's use of it here was admittedly a bit extra.
- A brief introduction to perturbation theory.
  - Suppose we seek to solve an equation
    $$f(x, \epsilon) = 0$$
    where ϵ is small.
  - We can approximate the solution in the form
    $$f^{(0)}(x) + f^{(1)}(x)\epsilon + f^{(2)}(x)\epsilon^2 = 0$$
    where the digit superscripts in parentheses just denote different functions, not derivatives or anything like that. For example, we could equally well have used the notation f, g, h; it's just that this is less general.
  - To solve the original equation, we first solve
    $$f^{(0)}(x_0) = 0$$
    for x_0.
  - Then we solve
    $$f^{(0)}(x_0 + \epsilon x_1) + \epsilon f^{(1)}(x_0) = 0$$
    for x_1.
  - Continuing in this fashion, our solution takes on the following form and is progressively refined as more terms are calculated.
    $$x = x_0 + \epsilon x_1 + \epsilon^2 x_2 + \cdots$$

7.3 Spherically Symmetric Harmonic Oscillator

2/14:

- Review.
  - Recall that the 3D case we're considering corresponds to the Hamiltonian
    $$\hat{H} = -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \frac{M\omega^2}{2}(x^2 + y^2 + z^2)$$
    - For this Hamiltonian, we are trying to solve the Eigenvalue equation
      $$\hat{H}\psi(x, y, z) = E\psi(x, y, z)$$
    - The solution may be obtained in Cartesian coordinates as a limiting case of the asymmetric harmonic oscillator, i.e., via the separation of variables
      $$\psi(x, y, z) = X(x)Y(y)Z(z)$$

- This results in the solutions

$$\psi(x,y,z)=\prod_{i=1}^{3}H_{n_i}(\xi_i)\mathrm{e}^{-\xi_i^2/2}c_{n_i} \qquad E_{n_1n_2n_3}=\hbar\omega\left(n_1+n_2+n_3+\frac{3}{2}\right)$$

  where $\xi_i=x_i\sqrt{m\omega/\hbar}$ and $x_1,x_2,x_3=x,y,z$, respectively.

– Recall also the polar coordinates r,θ,ϕ. The solution may be obtained here as well.

- In polar coordinates, we can see that the potential described above is central.
- Thus, we have that

$$\hat{\vec{L}}^{\,2}Y_{\ell m}(\theta,\phi)=\hbar^2\ell(\ell+1)Y_{\ell m}(\theta,\phi)$$

  and

$$\hat{L}_zY_{\ell m}(\theta,\phi)=\hbar mY_{\ell m}(\theta,\phi)$$

  and

$$-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2}{\mathrm{d}r^2}[U_{n\ell}(r)]+\underbrace{\left[V(r)+\frac{\hbar^2\ell(\ell+1)}{2Mr^2}\right]}_{V_{\mathrm{eff}}(r)}U_{n\ell}(r)=E_{n\ell}U_{n\ell}(r)$$

  where $-\ell\leq m\leq\ell$ and thus there is a $2\ell+1$ degeneracy of $E_{n\ell}$ associated with different m.
  - ➢ Recall that

$$R_{n\ell}(r)=\frac{U_{n\ell}(r)}{r}$$

- Substituting in

$$V(r)=\frac{M\omega^2r^2}{2}$$

  we obtain the effective potential described in Figure 7.1.
- Limiting cases then lead us to construct the ansatz

$$U_{n\ell}=f_{n\ell}r^{\ell+1}\mathrm{e}^{-M\omega r^2/2\hbar}$$

- Now propose that

$$f_{n\ell}(r)=\sum_j a_jr^j$$

- Recall that we may obtain the differential equation

$$f''_{n\ell}+2\left(\frac{\ell+1}{r}-\frac{M\omega r}{\hbar}\right)f'_{n\ell}+\left[\frac{2ME_{n\ell}}{\hbar^2}-\frac{(2\ell+3)M\omega}{\hbar}\right]f_{n\ell}=0$$

- We must set $a_1=0$.
- Moving on, we obtain

$$\sum_j j(j-1)a_jr^{j-2}+2\left(\frac{\ell+1}{r}-\frac{M\omega r}{\hbar}\right)\sum_j ja_jr^{j-1}+\left[\frac{2ME_{n\ell}}{\hbar^2}-\frac{(2\ell+3)M\omega}{\hbar}\right]\sum_j a_jr^j=0$$

- We now begin on new content, continuing the same derivation from above.
- We can further simplify the above equation by solving for a_{j+2} in terms of a_j.

– Begin by bringing all r's into the summations and running all sums from 0 to ∞ with no terms that go to zero so that every term is in r^j.

$$\sum_{j=0}^{\infty}(j+2)(j+1)a_{j+2}r^j+2(\ell+1)\sum_{j=0}^{\infty}(j+2)a_{j+2}r^j-\frac{2M\omega}{\hbar}\sum_{j=0}^{\infty}ja_jr^j+\left[\frac{2ME_{n\ell}}{\hbar^2}-\frac{(2\ell+3)M\omega}{\hbar}\right]\sum_{j=0}^{\infty}a_jr^j=0$$

- Combine the summations.

$$\sum_{j=0}^{\infty}\left[(j+1)(j+2)a_{j+2}+2(j+2)(\ell+1)a_{j+2}-\frac{2jM\omega}{\hbar}a_j+\frac{2ME_{n\ell}}{\hbar^2}a_j-\frac{(2\ell+3)M\omega}{\hbar}a_j\right]r^j=0$$

- Simplify and combine terms.

$$\sum_{j=0}^{\infty}\left[(j+2)(j+2\ell+3)a_{j+2}+\left(\frac{2ME_{n\ell}}{\hbar^2}-\frac{M\omega}{\hbar}(2j+2\ell+3)\right)a_j\right]=0$$

- Because each term in the above summation is affixed to a different power of r, meaning that no two terms can cancel, not only is the entire sum above equal to zero, but each individual term in it is equal to zero, too.
- Thus, for all $j\in\mathbb{Z}_{\geq 0}$,

$$0=(j+2)(j+2\ell+3)a_{j+2}+\left(\frac{M\omega}{\hbar}(2j+2\ell+3)-\frac{2ME_{n\ell}}{\hbar^2}\right)a_j$$
$$a_{j+2}=\frac{\frac{2ME_{n\ell}}{\hbar^2}-\frac{M\omega}{\hbar}(2j+2\ell+3)}{(j+2)(j+2\ell+3)}a_j$$

- This combined with the fact that $a_1=0$ means that *all odd a_j equal zero.*
  - It follows that $f_{n\ell}$ can be viewed as a function of r^2, not just r, since this fact means that the power series will be of the form

$$f_{n\ell}(r)=a_0+a_2r^2+a_4r^4+a_6r^6+\cdots+a_{2n}r^{2n}+\cdots$$

- Now observe that in the limit of large j (i.e., as $j\to\infty$),

$$a_{j+2}\approx\frac{\frac{M\omega}{\hbar}(2j)}{j^2+2j}$$

and thus[1]

$$f_{n\ell}(r)\approx \mathrm{e}^{M\omega r^2/\hbar}$$

  - This, in turn, would lead to an exponential growth of $U_{n\ell}$ as $r\to\infty$ and hence a non-renormalizable solution.
  - Consequently, there must be some maximum value of j which we will denote by $n:=j_{\max}$.
  - In particular, n will be the value of j such that the numerator of the expression above giving $a_{j+2}(a_j)$ equals zero. This will guarantee that $a_{n+2}=0$ and hence all $a_j=0$ for $j>n$.
  - Solving for this n, we have that

$$\frac{2ME_{n\ell}}{\hbar^2}=\frac{M\omega}{\hbar}(2n+2\ell+3)$$
$$E_{n\ell}=\hbar\omega\left(n+\ell+\frac{3}{2}\right)$$

    - Recall that n is even; $n\geq 0$; $\ell\geq 0$; and for each ℓ, we have $2\ell+1$ solutions with $-\ell\leq m\leq\ell$ where $\hbar m$ are the eigenvalues of $\hat{L}_z$.

- Notice the remarkable similarity between the energy equations for the spherically symmetric harmonic oscillator in Cartesian coordinates (left below) and polar coordinates (right below).

$$E_{n_1n_2n_3}=\hbar\omega\left(\bar{n}+\frac{3}{2}\right)\qquad\qquad E_{\bar{n}}=\hbar\omega\left(\bar{n}+\frac{3}{2}\right)$$

[1] How did we get this transformation to exponential growth??

  - On the left above, $\bar{n} = n_1 + n_2 + n_3$. On the right above, $\bar{n} = n + \ell$.

- Now let's investigate some particular solutions in both cases.
- $\bar{n} = 0$.
  - Cartesian: The only possible values are $n_1 = n_2 = n_3 = 0$, corresponding to
$$\mathrm{e}^{-M\omega(x^2+y^2+z^2)/2\hbar}$$
  - Polar: The only possible values are $n = \ell = 0$, corresponding to
$$\mathrm{e}^{-M\omega r^2/2\hbar}$$
  - In both cases, there is only one solution, and the solutions are mathematically equivalent.
- $\bar{n} = 1$.
  - Cartesian: We could have $n_1 = 1$, $n_2 = n_3 = 0$; $n_2 = 1$, $n_1 = n_3 = 0$; or $n_3 = 1$, $n_2 = n_3 = 0$; corresponding to
$$x\mathrm{e}^{-M\omega r^2/2\hbar} \qquad y\mathrm{e}^{-M\omega r^2/2\hbar} \qquad z\mathrm{e}^{-M\omega r^2/2\hbar}$$
  - Polar: We have $n = 0$; $\ell = 1$; and $m = 1$, $m = 0$, or $m = -1$; corresponding to
$$r\mathrm{e}^{-M\omega r^2/2\hbar}\underbrace{\sin\theta \mathrm{e}^{i\phi}}_{(x+iy)/r} \qquad r\mathrm{e}^{-M\omega r^2/2\hbar}\cos\theta \qquad r\mathrm{e}^{-M\omega r^2/2\hbar}\underbrace{\sin\theta \mathrm{e}^{-i\phi}}_{(x-iy)/r}$$
  - In both cases, there are three solutions, and the solutions are mathematically equivalent (up to linear combinations).
- A pattern is emerging: Naturally, it makes sense that the coordinate system chosen should not affect the solutions.
- $\bar{n} = 2$.

n_1	n_2	n_3
0	0	2
0	2	0
2	0	0
0	1	1
1	0	1
1	1	0

(a) Cartesian coordinates.

n	ℓ	m
0	2	2
0	2	1
0	2	0
0	2	-1
0	2	-2
2	0	0

(b) Spherical coordinates.

Table 7.1: Spherically symmetric harmonic oscillator solutions ($\bar{n} = 2$).

  - In both cases, there are six solutions.
  - Note that we do not consider the case where $n = \ell = 1$ in Table 7.1b because this would mean that $j_{\max} = n = 1$ is an odd number, which is not allowed.

7.4 Hydrogen Atom: Energy Eigenvalues and Eigenstates

2/16:

- Today: The hydrogen atom.
- The central potential is
$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$
- The problem is an electron revolving around a proton.
- The proton and electron have very different masses.
$$M_p c^2 \approx 1\,\text{GeV} \qquad\qquad m_e c^2 \approx 511\,\text{keV}$$
  - The ratio is
$$\frac{M_p}{m_e} \approx 2000$$
  - This justifies assuming that the proton is fixed (the Born-Oppenheimer approximation).
- The relevant Schrödinger equation is
$$-\frac{\hbar^2}{2m_e}\vec{\nabla}^2\psi_{n\ell m}(r,\theta,\phi) - \frac{e^2}{4\pi\epsilon_0 r}\psi_{n\ell m}(r,\theta,\phi) = E_{n\ell}\psi_{n\ell m}(\theta,\phi)$$
  - Note that E does not depend on m because m corresponds to the $2\ell+1$ degeneracy in energy.
    - Moreover, m only specifies orientation in space, which should intuitively not affect energy because space is isotropic and affine.
    - This is something we should absolutely know!!
  - Recall that
$$\begin{aligned}\psi_{n\ell m}(r,\theta,\phi) &= R_{n\ell}(r)Y_{\ell m}(\theta,\phi)\\ \hat{\vec{L}}^2 Y_{\ell m}(\theta,\phi) &= -\hbar^2\ell(\ell+1)Y_{\ell m}(\theta,\phi)\\ \hat{L}_z Y_{\ell m}(\theta,\phi) &= \hbar m Y_{\ell m}(\theta,\phi)\end{aligned}$$
  - Recall also polar coordinates
$$\begin{aligned}z &= r\cos\theta\\ x &= r\sin\theta\cos\phi\\ y &= r\sin\theta\sin\phi\end{aligned}$$
- Making the substitution
$$U_{n\ell}(r) = rR_{n\ell}(r)$$
can simplify the Schrödinger equation to the following equivalent effective potential and 1D problem.
$$-\frac{\hbar^2}{2m_e}\frac{\mathrm{d}^2}{\mathrm{d}r^2}[U_{n\ell}(r)] + \left[\frac{\hbar^2\ell(\ell+1)}{2m_e r^2} - \frac{e^2}{4\pi\epsilon_0 r}\right]U_{n\ell}(r) = E_{n\ell}U_{n\ell}(r)$$
  - This is the problem that started the whole game of quantum mechanics; it has enormous consequences in particle physics.
- As with the discussion associated with Figure 7.1, we have two competing potentials here (see Figure 7.2).
  - We are interested in finding the **bound states**.

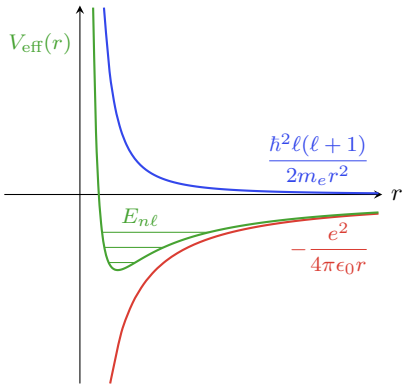


Figure 7.2: Hydrogen atom potential.

– In the limiting case that r is small ($r \to 0$), we can approximate the potential as with Figure 7.1 and take

$$U_{n\ell} \propto Cr^{\ell+1}$$

– In the limiting case that r is large ($r \to \infty$), we can approximate the potential as going to zero and take

$$U_{n\ell} \propto A\mathrm{e}^{\pm k_{n\ell} r}$$

where

$$|E_{n\ell}| = \frac{\hbar^2 k_{n\ell}^2}{2m_e}$$

– Thus, we combine the two partial solutions to propose the overall ansatz

$$U_{n\ell}(r) = f_{n\ell}(r) r^{\ell+1} \mathrm{e}^{-k_{n\ell} r}$$

- Note that we choose the negative exponent so the solution does not blow up at large r.

– Following the algebra in the notes, we obtain the following ODE determining $f_{n\ell}$.

$$f''_{n\ell}(r) + f'_{n\ell}(r)\left[\frac{2(\ell+1)}{r} - 2k_{n\ell}\right] + f_{n\ell}(r)\left[-\frac{2k_{n\ell}(\ell+1)}{r} + \frac{2m_e}{\hbar^2}\frac{e^2}{4\pi\epsilon_0 r}\right] = 0$$

- Aside: The prefactor to the rightmost $1/r$ term above (excepting the 2 coefficient) is typically written as follows.

$$\frac{m_e c}{\hbar}\frac{e^2}{4\pi\epsilon_0 \hbar c}$$

- The right fraction is the **electromagnetic fine structure constant**.
- Additionally, the other factor $\hbar/mc$ decomposes into $(h/m_e c)\cdot(1/2\pi)$ where we may recall from the first lecture that $h/m_e c$ is the **Compton wavelength** λ_c.
- The overall quantity is equal to the inverse of the **Bohr radius**.

– Thus, we can simplify the above equation to

$$f''_{n\ell}(r) + f'_{n\ell}(r)\left[\frac{2(\ell+1)}{r} - 2k_{n\ell}\right] + f_{n\ell}(r)\left[-\frac{2k_{n\ell}(\ell+1)}{r} + \frac{2}{a_{\mathrm{B}} r}\right] = 0$$

– As per usual, we propose that

$$f_{n\ell}(r) = \sum_j a_j r^j$$

and collapse functions that diverge.

- Substituting this power series into the differential equation, we obtain

$$\begin{aligned}0 &= \sum_j a_j r^{j-2} j(j-1) + \sum_j a_j j r^{j-1}\left[\frac{2(\ell+1)}{r} - 2k_{n\ell}\right] + \sum_j a_j r^j \left[-\frac{2k_{n\ell}(\ell+1)}{r} + \frac{2}{a_{\mathrm{B}} r}\right] \\ &= \sum_j a_j r^{j-1} j(j-1) + \sum_j a_j j r^{j-1}[2(\ell+1) - 2k_{n\ell} r] + \sum_j a_j r^j \left[-2k_{n\ell}(\ell+1) + \frac{2}{a_{\mathrm{B}}}\right] \\ &= \sum_j a_{j+1} r^j j(j+1) + \sum_j a_{j+1}(j+1) r^j 2(\ell+1) - \sum_j a_j j r^j k_{n\ell} 2 + \sum_j a_j r^j \left[-2k_{n\ell}(\ell+1) + \frac{2}{a_{\mathrm{B}}}\right]\end{aligned}$$

  - From line 1 to line 2, we multiplied through this function equal to zero by r.
  - From line 2 to line 3, we reindex some terms on the left from $j \to j+1$.
- It follows just like last class that

$$a_{j+1}(j+1)[j+2(\ell+1)] = a_j \left[2k_{n\ell} j + 2k_{n\ell}(\ell+1) - \frac{2}{a_{\mathrm{B}}}\right]$$

- Thus, we get that

$$a_{j+1} = \frac{k_{n\ell}(2j+2\ell+2) - \frac{2}{a_{\mathrm{B}}}}{(j+1)[j+2(\ell+1)]} a_j$$

- Once again, for similar reasons, there will also be some $j_{\max} = n$.
- Then

$$(n+\ell+1) k_{n\ell} = \frac{1}{a_{\mathrm{B}}}$$

  which means that

$$k_{n\ell} = \frac{1}{a_{\mathrm{B}}(n+\ell+1)}$$

- Then we get that

$$E_{n\ell} = -\frac{\hbar^2}{2m_e a_{\mathrm{B}}^2 (n+\ell+1)^2}$$

  where everything except the quantum numbers is the **Rydberg constant**.
- Consequently, in this case, we may define $\bar{n} = n + \ell + 1$.

- **Bound state**: A state in which the electron can escape to ∞.
  - We tend to suppress bound states so that the wave function does not have probability at ∞.
- **Electromagnetic fine structure constant**: The constant defined as follows. *Denoted by* $\boldsymbol{\alpha}$. *Given by*

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137}$$

- **Bohr radius**: The most probable distance from the nucleus of a hydrogen atom for its electron to exist. *Denoted by* $\boldsymbol{a_{\mathrm{B}}}$. *Given by*

$$a_{\mathrm{B}} = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \approx \frac{137}{2\pi}\lambda_c = 5.3 \times 10^{-11}\,\mathrm{m}$$

  - Note that we get the approximation from the aside's note that

$$a_{\mathrm{B}}^{-1} = \lambda_c^{-1} 2\pi\alpha$$

- **Rydberg constant**: The constant defined as follows. *Denoted by* **Ry**. *Given by*

$$\mathrm{Ry} = \frac{\hbar^2}{2m_e a_{\mathrm{B}}^2} = 13.6\,\mathrm{eV}$$

- Wagner is Argentenian.
- We'll continue on Monday.

Week 8

The Hydrogen Atom

8.1 Hydrogen Atom II

2/19:

- Review of the hydrogen atom.
  - The potential is given by
$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$
    - This is an important case of motion in a central potential in quantum mechanics.
  - We go to polar coordinates because they are most convenient for motion in a central potential.
  - We achieve separation of variables via
$$\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)Y_{\ell m}(\theta,\phi)$$
  - This leads into the spherical harmonics
$$\hat{\vec{L}}^2 Y_{\ell m}(\theta,\phi) = \hbar^2\ell(\ell+1)Y_{\ell m}(\theta,\phi)$$
$$\hat{L}_z Y_{\ell m}(\theta,\phi) = \hbar m Y_{\ell m}(\theta,\phi)$$
    - Additionally, the quantum number m satisfies $-\ell \leq m \leq \ell$, giving us $2\ell+1$ solutions for each ℓ.
  - With the spherical harmonics, the main question becomes how to find $R_{n\ell}$.
    - We do this via the change of variables
$$U_{n\ell}(r) = rR_{n\ell}(r)$$
      yielding a function that satisfies the analogous one-dimensional effective system
$$-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2}{\mathrm{d}r^2}[U_{n\ell}(r)] + \underbrace{\left[V(r) + \frac{\hbar^2\ell(\ell+1)}{2Mr^2}\right]}_{V_{\text{eff}}(r)} U_{n\ell}(r) = E_{n\ell}U_{n\ell}(r)$$
  - We analyze such systems using their asymptotic behavior as $r \to 0$ and $r \to \infty$.
    - See Figure 7.2. We are looking for bound states $E_{n\ell}$.
    - When the energy is positive, we have continuous solutions; it's only when the energy is negative that we have quantized bound states.
  - Performing such analyses, we propose an ansatz
$$U_{n\ell}(r) = f_{n\ell}(r)r^{\ell+1}\mathrm{e}^{-k_{n\ell}r}$$
    where
$$E_{n\ell} = -\frac{\hbar^2 k_{n\ell}^2}{2M}$$

– We suppose that f is a polynomial function

$$f_{n\ell}(r) = \sum_j a_j r^j$$

and solve for it using the differential equation

$$f''_{n\ell}(r) + f'_{n\ell}(r)\left[\frac{2(\ell+1)}{r} - 2k_{n\ell}\right] + f_{n\ell}(r)\left[-\frac{2k_{n\ell}(\ell+1)}{r} + \frac{2}{a_{\mathrm{B}} r}\right] = 0$$

– This analysis leads us to the recursion relation

$$a_{j+1} = \frac{2k_{n\ell}(j+\ell+1) - \frac{2}{a_{\mathrm{B}}}}{(j+1)(j+2\ell+2)} a_j$$

– We then choose $j_{\max} = N$, yielding

$$k_{n\ell} = \frac{1}{a_{\mathrm{B}} \underbrace{(N+\ell+1)}_{n}}$$

where we canonically call n the **principal quantum number**.

- This is a divergence from last time's notation, but one made for good reason, as we will see shortly.
- Note that we did not introduce this notation last time because we didn't want to have to discuss its subtleties then, as we will today.

– Thus, the energy depends only on this value n via

$$E_{n\ell} = -\frac{\hbar^2}{2m_e a_{\mathrm{B}}^2 (N+\ell+1)^2} = -\frac{\mathrm{Ry}}{n^2}$$

where Ry is the Rydberg constant defined last time.

- Essentially, the energy depends on this value n which in turn has a hidden dependence on ℓ.

- We now begin on new content, continuing from above however.
- The energy spacing versus n.

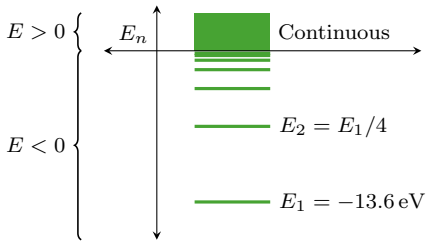


Figure 8.1: ^{1}H energy spacing vs. n.

– The energies get closer and closer together as n increases until they become continuous for positive values of energy.

– The equations and figure imply that $-E_1 = \mathrm{Ry}$ is the minimum energy necessary to remove the electron from the hydrogen atom.

– If we don't have this much energy, a lesser amount will still affect the electron, just moving it to an **excited state**.

    - In particular, $E_m - E_1$ is the amount of energy necessary to move the electron to an excited state E_m of higher energy than E_1.
  - What is also interesting is that if the electron is in an excited state of energy E_m, then it will *not* stay there forever.
    - Experimentally, even in this time independent potential, the electron can jump back down to a lower state by emitting electromagnetic radiation of energy $E_\gamma = E_m - E_1$.
    - This is evidence that the vacuum in which we assume the hydrogen atom lies is not really *vacuum*! Rather, the vacuum contains something called the EM field, and there are fluctuations in this EM field that can push the electron down energy states.
    - This is discussed more in Quantum Mechanics II, but is ignored in our present formalism of the hydrogen atom.

- Now for every fixed n, the equation $n = N + \ell + 1$ implies that $\ell = 0, 1, \ldots, n-1$.
  - But for every ℓ, there are $2\ell + 1$ solutions with the same energy.
  - Thus, for every n, there are

$$\sum_{\ell=0}^{n-1}(2\ell+1) = 2\sum_{\ell=0}^{n-1}\ell + \sum_{\ell=0}^{n-1}1 = 2\cdot\frac{n(n-1)}{2} + n = n^2$$

    different states with the same energy.

- Aside: A fun application of this stuff to cosmology.
  - The universe started as a hot plasma that cooled down as the universe expanded.
  - The early universe contained a lot of crap, including photons.
  - When early protons and electrons tried to combine at hot temperatures, the huge amount of EM radiation would kick the electrons out.
  - Thus, stable atoms could not form.
  - The specific temperatures at which this would occur were

$$k_\mathrm{B}T > 13.6\,\mathrm{eV}$$

  - At temperatures $k_\mathrm{B}T < 13.6\,\mathrm{eV}$, protons and electrons bind together, and the universe becomes transparent to radiation.
  - Evidence that this happened: Cosmic microwave background.
    - When the universe became transparent, it was at microwave temperatures.
    - This was when the universe was about 13 000 years old.

- Now back to math.

- Since we now have an explicit definition for $k_{n\ell}$, we may rewrite the solutions as

$$U_{n\ell}(r) = f_{n\ell}(r)r^{\ell+1}\mathrm{e}^{-r/a_\mathrm{B}n}$$

  - Notationally, do remember that n gives energy, ℓ gives angular momentum, and $N = n - \ell - 1$ gives the polynomial degree of $f_{n\ell}(r)$.

- Thus, if $N = 0$, then $n = \ell + 1$ and the radial probability density of finding the particle at a given r is

$$r^2|R_{n\ell}(r)|^2 = |U_{n\ell}(r)|^2 = r^{2n}\mathrm{e}^{-2r/a_\mathrm{B}n}$$

- What is the maximum, i.e., the most probable distance from the nucleus?

– Differentiate the probability density with respect to r and determine where it equals zero.

$$0 = 2nr^{2n-1}\mathrm{e}^{-2r/a_\mathrm{B}n} - \frac{2r^{2n}}{a_\mathrm{B}n}\mathrm{e}^{-2r/a_\mathrm{B}n}$$
$$\frac{2r^{2n}}{a_\mathrm{B}n} = 2nr^{2n-1}$$
$$r_\mathrm{max} = a_\mathrm{B}n^2$$

- What happens if you have an ion of charge Ze?
  – Then
  $$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$
  – Thus,
  $$E_n = -\frac{\mathrm{Ry}\, Z^2}{n^2}$$
  and the Bohr radius halves.

References

Griffiths, D. J., & Schroeter, D. F. (2018). *Introduction to quantum mechanics* (Third). Cambridge University Press.

Landau, L. D., & Lifshitz, E. M. (1977). *Quantum mechanics: Non-relativistic theory* (Third). Elsevier Butterworth-Heinemann.

Townsend, J. S. (2012). *A modern approach to quantum mechanics* (Second). University Science Books.