

8.04: Quantum Physics I (OCW)

Lecturer: Professor Barton Zwiebach

Notes by: Andrew Lin

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Fact 1

These notes were taken for my own preparation for the 8.04 Advanced Standing Exam, and they are transcribed from video lectures found on the [Spring 2016 OCW page](#). As a result, some content may be less complete than in an ordinary course (because recitations aren't available on OCW). The main reason for these notes' existence is to provide more continuity into my 8.05 and 8.06 notes from previous semesters.

Lecture 1: Overview of Quantum Mechanics

Quantum mechanics is a subject that takes time to learn, and we'll start by giving some perspective (explaining where we're going, introducing the basic features and ideas, and describing what's surprising about quantum mechanics). The subject is almost a hundred years old now, and officially we can think of the subject as starting in 1925, which was the year where Schrodinger and Heisenberg wrote down the equations of quantum mechanics. But the ideas really began earlier – the fundamental puzzles that led to quantum mechanics came from the end of the 19th century (Planck) and the beginning of the 20th century (Einstein and others).

Fact 2

Quantum mechanics should be thought of as a **framework to do physics** which has replaced classical mechanics as the “correct” description at the fundamental level. While classical mechanics provides a good approximation at everyday scales, we know that it breaks down at some point, and thus the way things really work are conceptually very different from what our intuition tells us.

What this course (and the ones after this) will do is take the principles and the framework of quantum mechanics and apply them to different physical phenomena, like quantum electrodynamics, quantum chromodynamics, quantum optics, and quantum gravity. In today's lecture and a bit of the next, we'll cover five introductory ideas: **linearity** of quantum mechanics, the necessity of **complex numbers**, the laws of **determinism**, interesting features of **superposition**, and the concept of **entanglement**.

The first idea, **linearity**, is important whenever we're considering a physical theory. Such theories have dynamical variables that we'd like to measure (because they are connected with values of physical observations) which are tied to certain **equations of motion**.

Example 3

Maxwell's theory of electromagnetism is a linear theory, meaning that if we have two different solutions to Maxwell's equations (such as two plane waves traveling in different directions), their sum (two plane waves propagating simultaneously) is also a valid solution.

In other words, solutions don't "affect" each other, and in practice this is useful because (for example) the air around us is constantly filled with electromagnetic waves. But linearity tells us that a single phone cable can transmit many phone calls at once, and it also tells us that if we're doing an electromagnetism experiment, it's okay to have other electromagnetic waves around us in the air.

Let's rigorize this discussion a bit more: in Maxwell's theory, we have the variables $(\vec{E}, \vec{B}, \rho, \vec{J})$ which must satisfy Maxwell's equations. What linearity tells us is that $(\alpha\vec{E}, \alpha\vec{B}, \alpha\rho, \alpha\vec{J})$ (for any real number α) will then also be a solution to the equations of motion, and if $(\vec{E}_1, \vec{B}_1, \rho_1, \vec{J}_1)$ and $(\vec{E}_2, \vec{B}_2, \rho_2, \vec{J}_2)$ are both solutions, then so is their sum $(\vec{E}_1 + \vec{E}_2, \vec{B}_1 + \vec{B}_2, \rho_1 + \rho_2, \vec{J}_1 + \vec{J}_2)$. We haven't written out Maxwell's equations explicitly, but we'll mention instead that the fundamental concept necessary for linearity is to write an equation schematically as

$$Lu = 0,$$

where u is some unknown and L is a **linear operator**. More generally, we can have multiple equations of this form, and u can be a vector of unknowns instead, but what's really important is that L satisfies the two properties of a linear operator:

$$L(au) = aLu, \quad L(u_1 + u_2) = Lu_1 + Lu_2.$$

More generally, these two properties together tell us that

$$L(\alpha u_1 + \beta u_2) = L(\alpha u_1) + L(\beta u_2) = \alpha Lu_1 + \beta Lu_2,$$

so if u_1, u_2 are solutions, then $L(\alpha u_1 + \beta u_2) = \alpha \cdot 0 + \beta \cdot 0 = 0$, and thus **any linear combination of solutions is also a solution** when we have a linear theory.

Example 4

The differential equation $\frac{du}{dt} + \frac{1}{\tau}u = 0$ can be written in the form $Lu = 0$ by taking L to be the linear operator $Lu = \frac{du}{dt} + \frac{1}{\tau}u$ (which we will also write in the form $L = \frac{d}{dt} + \frac{1}{\tau}$).

We can indeed check that this operator L above is linear by verifying the two properties of linearity: indeed,

$$L(au) = \frac{d}{dt}(au) + \frac{1}{\tau}(au) = a\frac{d}{dt}u + a\frac{1}{\tau}u = aLu,$$

and the other property follows in a similar manner.

Fact 5

Linear theories are generally much simpler than nonlinear theories (for example, Maxwell's theory is linear, while Einstein's theory of general relativity is very nonlinear and very complicated).

However, **classical mechanics is actually very nonlinear** (for example, Newton could solve the two-body problem but not the three-body one), and we can see this through the following example:

Example 6

Consider the classical motion of a one-dimensional particle under the influence of a potential $V(x)$; the equation of motion for the dynamical variable is then Newton's second law,

$$m \frac{d^2x(t)}{dt^2} = -V'(x(t)).$$

(Note that V' will always denote the derivative of V with respect to its argument.) The issue is that the left-hand side has a linear operation (taking two derivatives), but the right-hand side may not be linear because $V(x)$ can take an arbitrary form (for example, if $V(x) \propto x^3$, then $V'(x) \propto x^2$ is not linear). And this finally leads us to our discussion point for this class: **quantum mechanics is a linear theory**, in which the dynamical variable is a **wavefunction** Ψ (which can depend on time t and other variables), describing the dynamics of a quantum system over time. The equation that governs Ψ is then the **linear Schrodinger equation**

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi,$$

where \hat{H} is the **Hamiltonian** (which is a linear operator). In other words, we can write $L\Psi = i\hbar \frac{\partial \Psi}{\partial t} - \hat{H}\Psi = 0$ (where because derivatives are linear operations and \hat{H} is linear, L is also linear). We then have the advantage (over classical mechanics) that whenever we have solutions in quantum mechanics, we can scale and add them together. And as we go through this course, we'll see that the quantum mechanics solutions are indeed simpler and more elegant than the classical mechanics ones.

Fact 7

The \hbar on the left-hand side of the Schrodinger equation is the **reduced Planck's constant** (pronounced "h-bar"), originating from when Planck tried to fit the blackbody spectrum and needed a constant. And the Hamiltonian \hat{H} is for us to invent or discover (it depends on the physical characteristics of our system).

The physical interpretation of the wavefunction Ψ was not obvious for those who first invented quantum mechanics; Max Born later found that it had to do with probability, but we'll discuss this soon.

For now, we'll first turn to our second idea, which is the role of **complex numbers** in quantum mechanics. Schrodinger's equation above includes the constant $i = \sqrt{-1}$ – such complex numbers were originally invented because they were necessary for solving some equations (like $x^2 + 1 = 0$), and it turns out that "no more numbers need to be invented" after that to solve polynomial equations.

Definition 8

A **complex number** is of the form $z = a + ib$, where $a, b \in \mathbb{R}$ are real numbers and $i = \sqrt{-1}$. We define the **real part** of z to be $\text{Re}(z) = a$, the **imaginary part** of z to be $\text{Im}(z) = b$, the **complex conjugate** of z to be $z^* = a - ib$, and the **norm** of z to be $|z| = \sqrt{a^2 + b^2}$. The set of complex numbers is denoted \mathbb{C} .

We often represent complex numbers on the **complex plane**, identifying the point $a + ib$ with (a, b) in the xy -plane (so that the horizontal axis represents real part, and the vertical axis represents imaginary part). The norm of z is then given by the ordinary Euclidean distance formula, and we have

$$|z|^2 = a^2 + b^2 = zz^*,$$

which will be pretty important for us as we progress through this course. Notice that by trigonometry, if we want to find the complex number of norm 1 at an angle θ (counterclockwise from the x -axis), we have

$$z = \cos \theta + i \sin \theta$$

(because the real and imaginary parts are just the horizontal and vertical projections). What's important and nontrivial is that we also have **Euler's formula**

$$\cos \theta + i \sin \theta = e^{i\theta},$$

which we'll see come up as we work more with the equations of motion.

We may have seen complex numbers being used in classical mechanics and in electromagnetism, but they have always been used in auxiliary manners (because positions, velocities, electric fields, and other dynamical variables are always real-valued). But in quantum mechanics, Ψ must be complex-valued because the Schrodinger equation has an i in it (after all, if Ψ were real-valued, the left-hand side would be imaginary and the right-hand side would be real, which could only occur if both sides were 0). And yet, we can never measure complex numbers – any measurement we perform in a lab gives us a real number, and now we come to the point where we explain that **$|\Psi^2|$ is the physically relevant quantity** which is proportional to the probability of our systems being in a given configuration.

Remark 9. *Many physicists disliked or didn't believe this **Born interpretation** – Schrodinger's cat was actually a thought experiment designed to explain that this interpretation was ridiculous. And there were even papers at the time by famous physicists, like the EPR paper, which were later proven wrong. But when very good physicists are wrong, there's still a lot we can learn from them and a lot of interesting physics that results from the discussion.*

With that, we'll turn to a discussion of **determinism** which must come up when we talk about probabilities. Einstein was the one who (reluctantly) came up with the idea that light is quantized as **photons** (so not only can we observe light as an electromagnetic **wave**, we can also see it as a **particle** through the photoelectric effect). But the difference between a Newtonian and quantum particle is that the former has zero mass and carries a precise energy, position, and momentum, while the latter is some indivisible amount of propagating energy or momentum. So a photon is a quantum mechanical particle in the sense that it is a packet that cannot be decomposed further into smaller packets.

What Einstein found was that for any photon, we have the relation

$$E = h\nu,$$

where ν is the frequency of the light (of which the photon is part of) and $h (= 2\pi\hbar)$ is **Planck's constant**.

Fact 10

Here, we should remember that $c = \nu\lambda$ for any light wave, and because h is very small, individual photons have very low energy. But our eyes are very good at detecting light – if we're in a completely dark room, we are perhaps able to detect as few as five photons.

Example 11

Consider what happens when a beam of light hits a **polarizer**, which is a material with a preferential direction (which we'll set to be the x -axis). Recall that this means that light linearly polarized along the x -axis will pass through, but light linearly polarized along the y -axis will all be absorbed.

In fact, that linearly polarized light in the x -direction that passes through the polarizer looks identical when it enters and when it exits (same frequency and wavelength, and thus same energy). But now suppose we send light into the

polarizer which is polarized at some angle:

$$\vec{E}_\alpha = E_0 \cos(\alpha)\hat{x} + E_0 \sin(\alpha)\hat{y}.$$

From our study of electromagnetism, we know that the component along the y -direction is absorbed, so after going through the polarizer, we just have $\vec{E}_\alpha = E_0 \cos \alpha \hat{x}$. But we know that the energy in an electric field is proportional to $|\vec{E}|^2$, so this tells us that (because the initial electric field has magnitude E_0 , and the final electric field has magnitude $E_0 \cos \alpha$) **the fraction of energy that passes through the polarizer** is $\cos^2 \alpha$. (This checks out for $\alpha = 0, \frac{\pi}{2}$.) But from the point of view of the photon, what this means is that for individual (identical) photons that hit a polarizer, we must see a fraction $\cos^2 \alpha$ of the photons pass through and a fraction $1 - \cos^2 \alpha$ of them get absorbed (since we can't have "half a photon" pass through, or else that would change the frequency of the light, which we know doesn't happen). Classical physics doesn't like the fact that sending identical particles into a physical situation may yield varying outcomes, but that is indeed what we must have in quantum physics: **identically prepared experiments may give different results**, and thus we lose predictability as long as photons exist.

There are a few ways that we could try to get around this debacle: for example, we could hypothesize that photons will or will not pass through the polarizer based on the interatomic structure of the interaction, but this was found to not be true after repeated experiments. Another suggestion was that there are in fact **hidden variables** that are unknown to us (which distinguish the photons but make them still look identical), and those hidden variables affect whether or not the photon passes through the polarizer. (In other words, quantum theory is not complete.) It sounds philosophical, to the point where it seems like we wouldn't be able to refute it without measuring these hidden variables, but in fact the **Bell inequality** proved that even with them, quantum mechanics could not be made deterministic.

Fact 12

The Bell experiment will be discussed more in 8.05, but the main idea is that we can design an experiment in which the hidden variables (under classical mechanics) would imply a certain inequality. Then this inequality was shown experimentally not to hold once the technology was good enough to run the experiment!

So in summary, determinism is lost: photons must either go through the polarizer or not, and we can only predict the **probability with which they go through**. To write down the wavefunction of a photon, we can think of the photon as being in one of several **states** (we will sometimes also use "vectors" or "wavefunctions" for this same term). The motivation is that we can scale or add vectors together, and that's also what we can do with solutions to our quantum equations. Dirac invented the notation $|x\rangle$ to represent a vector (where x is just some label that describes the particular state): for example, for our polarizer, we have the two possible states

$$|\text{photon}; x\rangle, \quad |\text{photon}; y\rangle.$$

Then linearity tells us that we can always create the linear combination of states

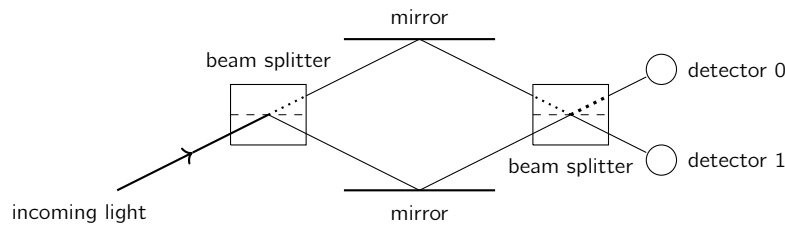
$$|\text{photon}; \alpha\rangle = \cos \alpha |\text{photon}; x\rangle + \sin \alpha |\text{photon}; y\rangle,$$

which is the quantum mechanical description of a photon polarized in the α -direction. Notice that this is similar to the classical $\vec{E}_\alpha = E_0 \cos(\alpha)\hat{x} + E_0 \sin(\alpha)\hat{y}$ in that we have the same $\cos \alpha$ and $\sin \alpha$ terms, but we no longer have the E_0 coefficient because we're now representing wavefunctions at the individual photon level. And **once the photon makes it through the polarizer**, its wavefunction is now just $|\text{photon}; x\rangle$.

That leads us to our next discussion of **superposition**. In classical physics, superposition tells us (for example) that we can add electric fields or force vectors, but in quantum physics we get something much stranger.

Example 13

Consider a **Mach-Zehnder interferometer**, which is a device with two beam splitters, two mirrors, and a detector, as shown below.



This device works in the following way: when incoming light hits each beam splitter, half of the light is reflected and half is transmitted. Those resulting light beams are reflected off of two mirrors to recombine at a second beam splitter, and after interference each detector will pick up some signal (in fact, we can adjust the system so that any fraction of the light, between 0 and 1 inclusive, goes to detector 0). Such a device was invented in the 1890s, and it is interesting to think about (given our discussion above) because we know that there must be something probabilistic going on at each beam splitter. In particular, if we have a superposition of different states, “some photons can go both up and down.” And in fact, when we say that there is an interference pattern being formed, it can’t be that different photons are interfering with each other (because energy can’t be created or destroyed); instead, **each photon interferes with itself**, and we can verify that this is what causes constructive or destructive interference by sending one electron into the device at a time.

More mathematically, we can say that each photon is in a superposition between the upper and lower beams in our diagram (where “upper beam” and “lower beam” are now our fundamental states). Remembering that we’re often associating the words “state,” “vector,” and “wavefunction” with each other, we’ll now explain how to associate physical properties with these superpositions. Suppose that we have two states $|A\rangle$ and $|B\rangle$, and suppose that we’re trying to measure **some particular property** (such as energy, spin, or position), so that measuring on $|A\rangle$ always gives some value a , and measuring on $|B\rangle$ always gives some value b . Then we can look at a quantum mechanical state of the form

$$|\Psi\rangle = \alpha|A\rangle + \beta|B\rangle$$

for complex numbers $\alpha, \beta \in \mathbb{C}$, which is a linear combination (superposition) of the states $|A\rangle$ and $|B\rangle$. If we measure that same property in $|\Psi\rangle$, what quantum mechanics tells us is that we will always get **either** the value a **or** the value b , but never something intermediate! This is very different from the situation we might have had in classical mechanics – instead of taking a weighted average (as we might be tempted to do), what $|\Psi\rangle$ really represents is that the probability of measuring a is proportional to $|\alpha|^2$, and the probability of measuring b is proportional to $|\beta|^2$, and those are the only two possibilities.

Example 14

Recalling the example state $|\text{photon}; \alpha\rangle = \cos \alpha |\text{photon}; x\rangle + \sin \alpha |\text{photon}; y\rangle$ we had above, we can think of the **polarizer as measuring the direction of polarization**: it will either measure that the photon is polarized in the x -direction (with probability $\cos^2 \alpha$) or that it is polarized in the y -direction (with probability $\sin^2 \alpha$).

And after we measure the state $\alpha|A\rangle + \beta|B\rangle$ once, that state will either **collapse** to the state $|A\rangle$ or the state $|B\rangle$, and future measurements will always return the same value – this is the **measurement postulate** of quantum

mechanics. (So if we wanted to know the original value of $|\Psi\rangle$ and didn't know α and β , we would need to prepare many identical copies of our setup and do our experiment many different times to assess the relevant probabilities).

Lecture 2: Superposition, Entanglement, and Interaction-Free Measurements

Last lecture, we started discussing superposition, and we explained that the superposition of two states does not have properties that are intermediate between the two initial states (instead, we obtain the properties of one of the two states with certain probabilities). This is the point at which we make a certain physical assumption: **superimposing a state with itself does not change the physics from just having the original state**. In other words,

$$|A\rangle \sim 2|A\rangle \sim -|A\rangle \sim i|A\rangle \sim \dots,$$

where we can put any nonzero coefficient in front of the fundamental state $|A\rangle$ and still have essentially the same object. So it makes sense to pick a convenient representative out of all of these, and typically that is the **normalized state** (which satisfies properties having to do with the norm of the state). We'll talk about this more later, but the reason we bring this up is to connect it more to our discussion of states of light from last time. If we think about our photon from last lecture with a superposition of x- and y-direction polarization, we can write it most generally as

$$\alpha |\text{photon}; x\rangle + \beta |\text{photon}; y\rangle,$$

where α, β are complex numbers and thus we have **four real parameters** to dictate the polarization direction. But we already know (and will review in a second) that there should only be **two** parameters to dictate the polarization of a particle, and our discussion of **normalization** helps us out here: if the overall constant doesn't matter, we can multiply the whole state by $\frac{1}{\alpha}$ to get a state of the (generic) form $|\text{photon}; x\rangle + \frac{\beta}{\alpha} |\text{photon}; y\rangle$, and thus all of the physics of a polarization state is contained in the ratio $\gamma = \frac{\beta}{\alpha}$ (which is a single complex parameter, corresponding to two real parameters). And indeed, the most general polarization of an electromagnetic wave is **elliptical** and dictated by two real parameters, the angle of its major axis and its eccentricity (since the overall size of the ellipse doesn't matter). This act of normalizing will come up again and again as we get farther into the course.

We'll emphasize one more important concept of superposition using **spins**.

Definition 15

Spin is a fundamental property of elementary particles, dictating their internal (intrinsic) angular momentum.

While no model of an elementary particle has ever been constructed where there is actually something inside spinning, there is indeed some angular momentum (even for a point particle), and spin is a very quantum mechanical property. Since angular momentum is a vector, we must decide the direction in which spin is pointing.

Example 16

Suppose we **measure spins along the z-direction**. Then if our particle is of **spin 1/2** (such as protons, neutrons, and electrons), we will either measure the particle in the **spin-up** or the **spin-down** state (corresponding to the respective direction of angular momentum).

Curiously, what we're saying is that whenever we measure the spin of a spin 1/2 particle, it is always either spin up (+1/2) or spin down (-1/2) with full magnitude. We'll denote the spin up and spin down states as $|\uparrow; z\rangle$ and $|\downarrow; z\rangle$,

respectively, and like in our earlier discussions, if those two are valid quantum mechanical states, so are states arising from superpositions such as

$$|\Psi\rangle = |\uparrow; z\rangle + |\downarrow; z\rangle.$$

(We won't talk about normalizing these states at the current moment; it's not too important.) So if we have a bunch of electrons which are in the state $|\Psi\rangle$ above, and we try to measure each of their spins in the z-direction, then we expect about half of the electrons to be spin up and about half to be spin down, due to the relative magnitude of the $|\uparrow; z\rangle$ and $|\downarrow; z\rangle$ terms.

But Einstein might ask the question of how we really know that the particles we measured were in the states $|\Psi\rangle$ – after all, our current setup does not help us distinguish between a system of all electrons in $|\Psi\rangle$, versus an ensemble of electrons where about half of them were in the state $|\uparrow; z\rangle$ to start with and the other half were in the state $|\downarrow; z\rangle$. This is what Einstein meant by **realism**: if we measure a particle to be spin-up, he would claim that this means the particle was spin-up to begin with. And we won't resolve this paradox until we learn more about spins (as we will later in the course). Instead, we'll just point out that if we had an ensemble where we had half spin-up and half spin-down particles, **we could take that ensemble and measure its spin along the x-direction instead**. It turns out that the particles in the $|\Psi\rangle$ state will all come out + along the x-direction, while the particles in the mixed ensemble will come out half-and-half + and -. So there is indeed an experiment that can tell whether these quantum states exist, and in fact they do.

This now prepares us to discuss the last of the fundamental introductory ideas for 8.04, which is **entanglement**. It turns out that two particles can become entangled without having strong interactions between them – they can even be non-interacting.

Example 17

Suppose particle 1 can be in one of the states $|u_1\rangle$ and $|u_2\rangle$, while particle 2 can be in the states $|v_1\rangle$ and $|v_2\rangle$. We wish to describe the states of the combined system of two particles.

To describe the overall system's state, it seems reasonable to specify each particle's state – for example, if particle 1 is in state $|u_1\rangle$ and particle 2 is in state $|v_1\rangle$, then we represent the whole system by the **tensor product** $|u_1\rangle \otimes |v_1\rangle$. In such a product, we always list the first particle's state on the left and the second particle's state on the right, so more generally we may have something that looks like

$$(\alpha_1 |u_1\rangle + \alpha_2 |u_2\rangle) \otimes (\beta_1 |v_1\rangle + \beta_2 |v_2\rangle).$$

Tensor multiplication then looks similar to regular multiplication, but we never move the states across the product: expanding and moving all of the constants out gives us

$$= \alpha_1 \beta_1 |u_1\rangle \otimes |v_1\rangle + \alpha_1 \beta_2 |u_1\rangle \otimes |v_2\rangle + \alpha_2 \beta_1 |u_2\rangle \otimes |v_1\rangle + \alpha_2 \beta_2 |u_2\rangle \otimes |v_2\rangle.$$

But notice that we can also be in a state that looks like

$$|u_1\rangle \otimes |v_1\rangle + |u_2\rangle \otimes |v_2\rangle,$$

which is a superposition of the states $|u_1\rangle \otimes |v_1\rangle$ and $|u_2\rangle \otimes |v_2\rangle$. But this time, we can't "factor" this state as a state of particle 1, tensored with a state of particle 2 – after all, matching coefficients with the general multiplication we did above would force $\alpha_1 \beta_1 = \alpha_2 \beta_2 = 1$ but $\alpha_1 \beta_2 = \alpha_2 \beta_1 = 0$, which is a contradiction (since $\alpha_1 \beta_1 \alpha_2 \beta_2$ would then have to be both 1 and 0). So we have an **unfactorizable state**, in which we cannot just describe the configuration as independently analyzing the first and second particle. In other words, we have an **entangled state** – knowing

something about the first particle tells us about the second and vice versa – even though no interactions have occurred between them!

Example 18

If we consider two spin 1/2 particles, then we can consider the entangled state

$$|\uparrow; z\rangle_1 \otimes |\downarrow; z\rangle_2 + |\downarrow; z\rangle_1 \otimes |\uparrow; z\rangle_2.$$

People often speak of “Alice and Bob” each having one of these two particles (arranged in their entangled state), with the idea being that Alice and Bob are very far away (perhaps one on Earth and the other on the moon). Then Alice and Bob share an entangled pair, and very interesting experiments can be done (in real labs, this can be done with two photons that are hundreds of kilometers apart), coming from the fact that the two particles’ properties are correlated in strange ways. For example, if Bob measures his particle and finds that it is spin-down, then the whole state must collapse into the $|\uparrow; z\rangle_1 \otimes |\downarrow; z\rangle_2$ state, meaning that if Alice also simultaneously measures her particle, she must find that it is spin-up (**even before** light has had time to travel from one of the entangled particles to the other). It turns out that this does **not** contradict special relativity – we cannot actually send any information through this process – but the collapse is still instantaneous.

Einstein would again object to this concept of entanglement, suggesting instead that some entangled pairs are really in the $|\uparrow; z\rangle_1 \otimes |\downarrow; z\rangle_2$ state while others are in the $|\downarrow; z\rangle_1 \otimes |\uparrow; z\rangle_2$ state. But that’s where Bell’s inequality comes in – if Alice and Bob can measure in three different directions, then the correlations that result are impossible to explain with classical physics. So what’s going on is really subtle and violates classical mechanics in a peculiar way.

Example 19

We’ll now return to the Mach-Zehnder interferometer from Example 13 and perform some further analysis.

Recalling that an arbitrary superposition of the top and bottom paths gives us a valid state for an incoming photon, we’ll represent that superposition with a **column vector** $\begin{bmatrix} \alpha \\ \beta \end{bmatrix}$ which give the probability amplitudes of being in the top and bottom paths. (These α, β may depend on time and position, and remember that their norm squared give the actual probabilities.) In particular, this is where we must do a **normalization**: since probabilities need to add to 1, we must have $|\alpha|^2 + |\beta|^2 = 1$. For example, $\begin{bmatrix} 1 \\ 0 \end{bmatrix}$ corresponds to being in the upper beam, and $\begin{bmatrix} 0 \\ 1 \end{bmatrix}$ corresponds to being in the lower beam. Then everything indeed works out: we have

$$\begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \alpha \begin{bmatrix} 1 \\ 0 \end{bmatrix} + \beta \begin{bmatrix} 0 \\ 1 \end{bmatrix},$$

so that our generic state is indeed a superposition of the “upper beam” and “lower beam” states. If we now think about our beam splitter, we know that an incoming photon from the top would produce some reflection amplitude s (to the top path) and some transmission amplitude t (to the bottom path), meaning that the beam splitter takes $\begin{bmatrix} 1 \\ 0 \end{bmatrix}$ to $\begin{bmatrix} s \\ t \end{bmatrix}$. (The values of s, t depend on the particular design of the beam splitter.) Clearly, we must have $|s|^2 + |t|^2 = 1$.

Similarly, a photon coming from the bottom results in a change from $\begin{bmatrix} 0 \\ 1 \end{bmatrix}$ to $\begin{bmatrix} u \\ v \end{bmatrix}$, where $|u|^2 + |v|^2 = 1$. In other

words, we need four numbers to characterize this beam splitter – indeed, for an arbitrary state $\begin{bmatrix} \alpha \\ \beta \end{bmatrix}$ passing through the beam splitter, **by linearity** we have that

$$\begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \alpha \begin{bmatrix} 1 \\ 0 \end{bmatrix} + \beta \begin{bmatrix} 0 \\ 1 \end{bmatrix} \mapsto \alpha \begin{bmatrix} s \\ t \end{bmatrix} + \beta \begin{bmatrix} u \\ v \end{bmatrix} = \begin{bmatrix} \alpha s + \beta u \\ \alpha t + \beta v \end{bmatrix} = \begin{bmatrix} s & u \\ t & v \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix}.$$

In other words, we can think of the beam splitter's action as **multiplying by a certain 2×2 matrix!** This perspective will be very useful for us going forward for a variety of reasons. For our purposes, we'll assume we have a **balanced** beam splitter where half of the light goes through and the other half is reflected, so that $|s|^2 = |t|^2 = |u|^2 = |v|^2 = \frac{1}{2}$. But that doesn't allow us to determine exactly what s, t, u, v are (because of the phase), and let's first make the **guess** that it is $\begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix}$. As long as this matrix satisfies probability conservation, there should theoretically exist a beam splitter that can perform that operation. But **this doesn't work** – after all, notice that

$$\begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix} \begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \end{bmatrix},$$

and the norm of our column vector has changed. Instead, it turns out one answer is $\begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{bmatrix}$; indeed,

$$\begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} \alpha + \beta \\ \alpha - \beta \end{bmatrix},$$

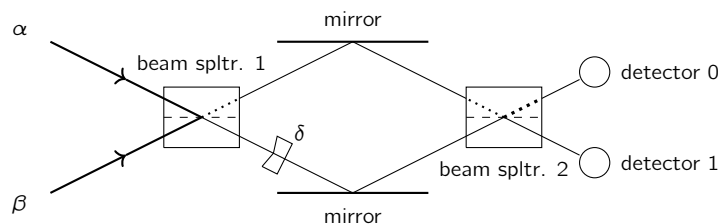
and this final vector indeed has the same norm as the initial one, because

$$\left| \frac{1}{\sqrt{2}}(\alpha + \beta) \right|^2 + \left| \frac{1}{\sqrt{2}}(\alpha - \beta) \right|^2 = \frac{1}{2}(\alpha + \beta)(\alpha^* + \beta^*) + \frac{1}{2}(\alpha - \beta)(\alpha^* - \beta^*),$$

at which point the cross-terms vanish and we're left with $\frac{1}{2}(2\alpha^2 + \beta^2) = \alpha^2 + \beta^2$, which is 1 by assumption. So this beam splitter matrix will do the job for us – it's not the only solution, and we'll consider two beam splitter matrices

$$BS_1 = \frac{1}{\sqrt{2}} \begin{bmatrix} -1 & 1 \\ 1 & 1 \end{bmatrix}, \quad BS_2 = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}.$$

corresponding to the two beam splitters in the diagram below. We may also suppose that along the bottom path (hitting the bottom mirror), we place a piece of glass which shifts the probability amplitude by a phase:



In other words, a probability amplitude of β will turn into a probability amplitude of $\beta e^{i\delta}$, where $\delta \in \mathbb{R}$. Since $|\beta| = |\beta e^{i\delta}|$, this preserves the norm of the probability amplitude. (We won't use this phase shifter in today's lecture, but it's still a useful concept that will come up in the future.)

Problem 20

Consider the setup in the diagram above without the phase shifter. What do we find at the detectors if we have an incoming state $\begin{bmatrix} \alpha \\ \beta \end{bmatrix}$?

We'll assume that the mirrors do not do anything to the column vector – in fact they each multiply a component by -1 , so overall that's just a constant shift which does nothing – meaning that the detector state comes from applying first the beam splitter matrix BS_1 , then the beam splitter matrix BS_2 . In other words, we have

$$\text{output} = (BS_2)(BS_1) \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \begin{bmatrix} -1 & 1 \\ 1 & 1 \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 0 & 2 \\ -2 & 0 \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \begin{bmatrix} \beta \\ -\alpha \end{bmatrix}.$$

Thus, if we send in a photon from the bottom (meaning that we start with the column vector $\begin{bmatrix} 0 \\ 1 \end{bmatrix}$), the output will be the column vector $\begin{bmatrix} 1 \\ 0 \end{bmatrix}$. In particular, this means that even after the photon split at beam splitter 1, there was an interesting interference at beam splitter 2 which caused the amplitudes to cancel out along detector 1 and combine along detector 0, such that **every photon** will be detected at the top detector! (And indeed, this interference pattern was detected in experiments.)

Problem 21

Next, consider the setup in the diagram above, but along the bottom path we place a wall of concrete (at the location of the phase shifter) so that light cannot pass through the bottom path. What do we find at the detectors if we have an incoming state $\begin{bmatrix} \alpha \\ \beta \end{bmatrix}$?

We can no longer use our matrix multiplication formula from above; instead, we'll look at calculation step by step. After passing through the first beam splitter, we are in the state

$$(BS_1) \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} -1 & 1 \\ 1 & 1 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix}.$$

However, along the bottom path, we **lose** the probability amplitude of $\frac{1}{\sqrt{2}}$ due to the concrete wall – in other words, the input into the second beam splitter is $\begin{bmatrix} \frac{1}{\sqrt{2}} \\ 0 \end{bmatrix}$ (nothing reaches the splitter from below). Thus, the final detected column vector is

$$(BS_2) \begin{bmatrix} \frac{1}{\sqrt{2}} \\ 0 \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \begin{bmatrix} \frac{1}{\sqrt{2}} \\ 0 \end{bmatrix} = \begin{bmatrix} \frac{1}{2} \\ \frac{1}{2} \end{bmatrix}.$$

Interestingly, this means that **by blocking some photons, we've created a signal at detector 1**, which may seem somewhat counterintuitive. (And in fact we'll see by the end of this lecture that this is even more unintuitive than we might initially think!) Remembering that the squared components correspond to the probabilities, we can summarize the results of Problem 20 and Problem 21 as follows:

| Outcome (open paths) | Probability |
|----------------------------------|-------------|
| Photon is detected at detector 0 | $1^2 = 1$ |
| Photon is detected at detector 1 | $0^2 = 0$ |

| Outcome (one blocked path) | Probability |
|----------------------------------|---|
| Photon ends at concrete block | $\left(\frac{1}{\sqrt{2}}\right)^2 = \frac{1}{2}$ |
| Photon is detected at detector 0 | $\left(\frac{1}{2}\right)^2 = \frac{1}{4}$ |
| Photon is detected at detector 1 | $\left(\frac{1}{2}\right)^2 = \frac{1}{4}$ |

We can take these values and put them into the following thought experiment:

Problem 22 (Elitzur-Vaidman bombs)

Consider a certain kind of bomb which detonates if a photon passes through it, and suppose that we have several of these bombs but that about half of them have gone defective (so that they will not detonate even if a photon passes through). How can we decide whether a bomb is working without breaking the components apart or having it explode?

In classical physics, this is clearly impossible – if we do the measurement to see if the bomb explodes, then either the bomb is defective or we have no more bomb left. But with the Mach-Zehnder interferometer system that we've just described, **we can indeed find a working bomb without having it explode!**

Solution. Place the bomb where our phase shifter is placed in our diagram above, such that a photon passing through the bottom path would set off the bomb. Then if the bomb is defective, it's as if both paths are open (see left table above), and thus photons must be detected at detector 0 (with probability 1). But if the bomb is working, then we've essentially put a block of concrete along the bottom path (with the extra effect that the bomb explodes in that situation). Thus (see right table above), half of the time the bomb will explode, but there is a $\frac{1}{4}$ chance that the bomb does not explode and the photon is detected at detector 0, and likewise also a $\frac{1}{4}$ chance that the bomb does not explode and the photon is detected at detector 1. Thus, whenever we see a photon at detector 1, we must have a working bomb which has still not detonated. \square

Fact 23

It turns out that adjusting the experiment (placing the bomb in a resonant cavity, for example) can give us arbitrarily high probabilities that the bomb will not go off before we find out that it works! And thus quantum mechanics indeed allows us to perform very surprising measurements.

Lecture 3: The Photoelectric Effect, Compton Scattering, and de Broglie Wavelength

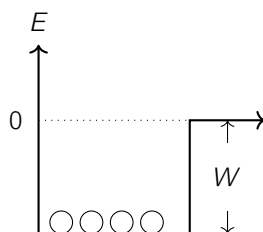
Last lecture, we discussed the Mach-Zehnder interferometer and what happens to it when we pass a photon through the device – essentially, a relatively simple calculation led to a very surprising result. We'll continue studying photons today, but we'll take a step back to 100 years ago, looking at how physicists came up with quantum mechanics through photons' behavior.

Fact 24

The **photoelectric effect** can be traced back to Hertz's experiment in 1887, in which high-energy beams of light were shined on polished metal plates and electrons (called **photoelectrons** because they are created in this way) were released, creating a **photoelectric current**.

The primary interesting feature that was observed was that there was always a certain threshold **critical frequency** ν_0 , above which a current is measured but below which nothing happens. And this threshold depended on the metal being irradiated, as well as the roughness and crystalline nature of the surface – it was later discovered that there are free electrons roaming around this crystalline structure, and the critical frequency ν_0 thus depends on how much energy is required to free an electron from the metal. Additionally, it was found that the intensity of the light governed the magnitude of the photoelectric current, but that this intensity does not affect the energy of the photoelectrons themselves! So the incoming energy beam affects the number of excited photoelectrons but not their energy – in fact, the energy of the photoelectrons has a **linear relation** with the frequency ν of the incoming light.

These properties are difficult to explain if we treat light solely as a wave, and Einstein's answer in 1905 was (as previously mentioned) that light must come in **quantized bundles of energy** (which were later named **photons** by Gilbert Lewis in the 1920s), with energy $E = h\nu$. The picture that we should have in mind is the following:



Essentially, this graphs the potential energy function for our electrons – while they are in the metal, they are stuck to it unless we can provide some potential energy to get them out of the well. Once we do this, the electron will be able to fly freely and not be affected by the metal.

Definition 25

For any surface, the **work function** (denoted W) is the energy needed to release an electron to the vacuum around the surface.

If Einstein's proposition about photons is correct, then that implies that the energy of a photoelectron satisfies

$$\frac{1}{2}mv^2 \approx E_{e^-} = E_\gamma - W = h\nu - W$$

(the energy of the photon is transferred to kinetic energy of the photoelectron, except the work function W). It wasn't until 1915 that this was verified experimentally by Millikan, and in fact that experiment gave an estimate of h within 1 percent of the accepted value today (which was the best up until that point). But even then, the photoelectric effect experiment wasn't enough on its own to really convince people that photons existed, because Maxwell's theory was very successful and accepting photons meant accepting loss of determinism and all of the other features of quantum physics we've been discussing.

Let's see an example computation to see what kind of setting we're dealing with:

Problem 26

Consider ultraviolet light of $\lambda = 290\text{nm}$ shined on a metal with work function $W = 4.05\text{ eV}$. What are the speed and energy of the emitted photoelectrons?

Solution. The idea is that we should be able to do this problem without needing to remind ourselves what “eV” means, or searching up the value of \hbar , and in general perform back-of-the-envelope estimates and calculations.

First of all, the energy of a photon is

$$E_\gamma = h\nu = \frac{hc}{\lambda} = \frac{2\pi\hbar c}{\lambda}$$

(using the definition of the reduced Planck’s constant), and it’s useful to remember that $\hbar c \approx 200\text{ MeV} \cdot \text{fm}$ (the actual number is 197.33), where $1\text{ fm} = 10^{-15}\text{ m}$ (fm stands for “fermi” or “femtometer”). Thus, we can simplify to

$$= \frac{2\pi \cdot 197\text{ MeV} \cdot 10^{-15}\text{m}}{290 \cdot 10^{-9}\text{ m}} = \frac{2\pi \cdot 197}{290}\text{ eV} = \boxed{4.28\text{ eV}}$$

(where the last step is the only one where we really need to do any calculation). Thus, the energy of the photon is

$$E_e = E_\gamma - W = 4.28\text{ eV} - 4.05\text{ eV} = 0.23\text{ eV},$$

and this is essentially a **nonrelativistic electron** because the rest mass of an electron is about 511 eV:

$$0.23\text{ eV} = \frac{1}{2}mv^2 = \frac{1}{2}m_e c^2 \left(\frac{v}{c}\right)^2 = \frac{1}{2} \cdot (511000\text{ eV}) \left(\frac{v}{c}\right)^2,$$

yielding $v \approx \boxed{284\text{ km/s}}$. □

We’ll talk a bit more about Planck’s constant directly: because it shows up in the equation $E_\gamma = h\nu$, it must have units

$$[h] = \frac{[E]}{[\nu]} = \frac{[M][L^2]/[T^2]}{1/[T]} = \frac{[M][L^2]}{[T]}$$

(where we’re working with units characterized by **mass** M , **length** L , and **time** T – that is all we need). We’ll rearrange this expression slightly to match with another physical quantity:

$$= [L] \cdot \frac{[M][L]}{[T]} = [r][p] = [\vec{L}];$$

in other words, **Planck’s constant has the same units as angular momentum!** This is something for us to keep in mind, and that’s why saying that we have a “particle of spin $\frac{1}{2}$ ” actually means that “the particle has intrinsic angular momentum $\frac{\hbar}{2}$.” (Unfortunately, as we go forward, we’ll need to be careful about the 2π factor between h and \hbar – we’ll use whichever one looks nicer in the present situation.) And the idea is that **once we have a new constant of nature**, like h or c or G , we can get inspired and **create new quantities with that constant**. Since $[h] = [r][p]$, we can invent an associated **length** for each particle depending on its **momentum** p (which we’ll do shortly), or even more simply do the following:

Definition 27

The **Compton wavelength** of a particle of mass m is $\lambda_c = \frac{h}{mc}$.

Example 28

The electron's Compton wavelength is

$$\lambda_c(e) = \frac{h}{m_e c} = \frac{2\pi\hbar c}{m_e c^2} = \frac{2\pi \cdot 197.33 \text{ MeV} \cdot \text{fm}}{0.511 \text{ MeV}} \approx 2426 \text{ fm} = 2.426 \text{ pm}.$$

For comparison, this is smaller than the Bohr radius of an electron (about 50 pm), but much larger than the size of a nucleus.

To understand the significance of this length that we've just defined, we'll see its use in both an experiment and a thought experiment:

Example 29

Suppose we have a particle of mass m . Then its associated rest mass (energy) is mc^2 , so a photon with the same energy as the particle has frequency $\nu = \frac{mc^2}{h}$ and thus wavelength $\frac{c}{\nu} = \frac{h}{mc} = \lambda_c$.

This actually has some experimental implications in high-energy particle physics: for example, if a photon hits an electron with a Compton wavelength equal to the wavelength of the light, then the comparable energy scales can create new particles. Thus, it is difficult to isolate a particle to length scales shorter than its Compton wavelength without causing damage to it!

Around the time that Einstein discovered general relativity, he was also thinking about photons again – throughout his life, he was very suspicious about the quantum theory and spent much of his time thinking about it. In 1916, he proposed that not only do these photons (which weren't yet called photons at the time) have energy, but they also serve as **quanta of momentum**. Specifically, there is a relativistic relation

$$E^2 - p^2 c^2 = m^2 c^4$$

between the energy and the momentum of a particle (this comes from the two formulas $E = \frac{mc^2}{\sqrt{1-\frac{v^2}{c^2}}}$ and $\vec{p} = \frac{m\vec{v}}{\sqrt{1-\frac{v^2}{c^2}}}$, which reduce to $E = \frac{1}{2}mv^2$ and $\vec{p} = m\vec{v}$ in the low-velocity limit). Thus, if we know the momentum and the energy of a particle, we also know its mass. Since **photons have zero mass**, we must have

$$m_\gamma = 0 \implies E_\gamma = p_\gamma c,$$

meaning that the photon momentum (treating light as a particle) is

$$\boxed{p_\gamma} = \frac{E_\gamma}{c} = \frac{h\nu}{c} = \boxed{\frac{h}{\lambda_\gamma}}.$$

This looks similar to the Compton wavelength relation, but it was still not strong enough evidence until **Compton scattering** was studied:

Example 30

Consider x-rays shining on atoms, where the incoming photons are comparably energetic (100 eV to 100 keV, while binding energies of atoms are on the order of 10 eV).

If these photons are high enough in energy, then the resulting excited electrons are almost as if they started off being free. In such a situation, we have a violation of the classical **Thompson scattering**, which was what caused

physicists to finally accept the wave-like nature of photons – those scattering phenomena could be calculated just like scattering phenomena of other particles.

In the classical case, we think of light as a wave, in which the magnetic field doesn't do very much (because we have a low-energy electron) and the electric field shakes the electron: the resulting cross-section is

$$\frac{d\sigma}{d\Omega} = \left(\frac{e^2}{mc^2} \right)^2 \frac{1}{2} (1 + \cos^2 \theta)$$

as a function of the angle θ between the incident angle of the wave and the direction that the photon is scattered in. If we haven't seen this kind of formula before, the units are area per solid angle, which is the same as just area; what this cross-section measures is, for a given solid-angle region $d\Omega$, the surface area $d\sigma$ from the incoming beam that scatters into that solid-angle. That area then corresponds to an energy (because a certain amount of energy from the electromagnetic wave goes into each area), and thus with all of this we get a formula for the **intensity of radiation** as a function of the solid angle. But another property of this classical case is that the frequency of the outgoing wave (after hitting the electron) is the same as the frequency of the incoming wave, because the electron is being driven at the same frequency as the light wave.

It turns out that at high energies, the result actually looks very different! If we treat a photon as a particle, so that we have a particle-particle collision, then both particles have some energy and momentum and we should use conservation laws. Before the collision, we have a photon of energy E and momentum p and an electron at rest, and after the collision both particles are moving. It's an exercise to show that the photon can't be observed by those conservation laws, and because the electron now has kinetic energy, the photon must lose some energy, meaning that $\lambda_f > \lambda_i$ (longer wavelength means lower energy), and in fact we have

$$\lambda_f = \lambda_i + \frac{h}{m_e c} (1 - \cos \theta)$$

where $\frac{h}{m_e c}$ is the Compton wavelength $\lambda_c(e)$ for the electron. In other words, if $\theta = 0$, the photon keeps going and basically doesn't kick the electron, resulting in no change. However, if the photon bounces totally backwards, then $\theta = \pi$ and the wavelength increases by $2\lambda_c$.

Fact 31

This Compton scattering experiment was in fact performed, and let's describe briefly how it was set up. Molybdenum X-rays with $\lambda = 0.0709$ nm (corresponding to an energy of $E_\gamma = 17.49$ keV) hit a piece of carbon foil. Then the relation between intensity and outgoing λ turns out to have **two peaks**: the smaller one occurs around $\lambda_i = 0.0709$ nm, while the larger peak occurs at $\lambda_f = 0.0731$ nm.

Noticing that the shift in wavelength is 0.0022 nm, this is pretty close to the Compton wavelength calculated in Example 28, meaning that the larger peak is indeed corresponding to what we expect (a shift on the order of λ_c). But the smaller peak needs slightly more explanation, and this is where **Louis de Broglie's** work of 1924 comes into consideration.

Treating light as both a particle and a wave means that it will have characteristics of both (light exhibits interference, but it also comes in packets), and de Broglie inferred that this must be a more general property – he took the fundamental step of claiming that **all matter particles behave as waves**, not just light. This is particularly interesting, because in his description, the wave that's being associated to light is not the electromagnetic wave – it's the **probability amplitude** wave (which are the numbers that we were tracking with the interferometer last lecture)! And that wavefunction was not known about yet, so what was being unsaid in the following conjecture was the question of "of what?" (that is, what is the wave made of).

Conjecture 32 (de Broglie (1924))

The wave-particle duality is universal for all matter: for each particle of momentum p , we have an associated **plane wave** of wavelength $\lambda_p = \frac{h}{p}$, known as the **de Broglie wavelength**.

At the time, there was no experimental evidence for the claim, but experiments came a few years later – it was seen that electrons could be diffracted in ways so that they would collide in lattices like waves! (We can read about the **Davisson-Germer experiment**, for example.) Over time, the two-slit diffraction experiment was performed with larger and larger particles – in fact, in the last few years, molecules of weight around 10000 atomic mass units have exhibited interference patterns. And we should remember that these interference patterns come from a particle's wavefunction interfering with itself! We'll see next lecture how this leads us to the Schrodinger equation and the wave-like nature of matter.

Lecture 4: de Broglie Waves, Propagation, and the Free Particle

Last time, we discussed de Broglie's conjecture of "matter waves," in which a free particle with momentum p is associated to a plane wave of de Broglie wavelength $\lambda_p = \frac{h}{p}$. It turns out that such a plane wave is actually the wavefunction of a free particle, and its wave equation is basically the Schrodinger equation! So this is really a pillar of quantum mechanics that we're working with, and the challenges when de Broglie's matter wave was first proposed came in what physical (e.g. directional) properties it encoded – it turns out that this wavefunction will tell us about **spin**.

But we'll start with the case where these directional properties don't matter much – in the case where we have an electron at low velocity or in a small magnetic field, we'll ignore the spin properties and just write the wavefunction $\Psi(\vec{x}, t)$ as being **complex-valued**. We're then (historically) curious whether Ψ is measurable and what its meaning is, but first let's consider what it actually means for a wave to have wavelength $\frac{h}{p}$ (inversely proportional to momentum).

Example 33

For simplicity, consider non-relativistic (Galilean) physics. Suppose that from our perspective, we have a particle of momentum p , and there is a "boosted observer" moving at constant velocity v relative to us. We wish to consider the differences in observed wavefunctions between the two observers.

Because $p = \frac{h}{\lambda} = \frac{h}{2\pi} \frac{2\pi}{\lambda}$, we can rewrite the momentum as $p = \hbar k$, where \hbar is the usual reduced Planck's constant and k is the **wavenumber** (the number of periods per unit distance). Call our frame S , and call the other frame S' ; fix the coordinates so that S' is moving with velocity v in the x -direction. Then after t seconds, the two frames are vt units apart, and our particle of mass m will have velocities \underline{v} and \underline{v}' in frames S and S' , respectively, and suppose that it has momenta p and p' respectively as well. We can now relate all of our coordinates with Galilean transformations (which are accurate enough for low velocities):

$$x' = x - vt, \quad t' = t.$$

Taking a time-derivative, we have $\frac{dx'}{dt'} = \frac{dx}{dt} - v$, so $\underline{v}' = \underline{v} - v$, which we expect from our usual concept of relative motion. Therefore,

$$p' = m\underline{v}' = m\underline{v} - mv = p - mv,$$

so the “moving observer” will see a **different** de Broglie wavelength of

$$\lambda' = \frac{h}{p'} = \frac{h}{p - mv} \neq \frac{h}{p} = \lambda.$$

But if this were a familiar propagating wave like a sound or water wave, the relation between λ and λ' would see a **Doppler shift** for the frequency, but the wavelength would not change! Indeed, consider an ordinary wave under Galilean transformations, and consider its **phase** $kx - \omega t$ (where k is the wavenumber and ω is the angular frequency). Waves can then be expressed as sines, cosines, or exponentials of this phase, and what's important is that **the phase of a wave is a Galilean invariant** (if two people look at the same point on a wave, then they will always agree on the value of that phase – for example, both observers will agree that the wave has a maximum or minimum at a particular point). In particular, we can write

$$\phi = k \left(x - \frac{\omega}{k} t \right) = \frac{2\pi}{\lambda} (x - Vt) = \frac{2\pi x}{\lambda} - \frac{2\pi V}{\lambda} t.$$

where we use the fact that $\frac{\omega}{k} = \frac{2\pi f}{2\pi/\lambda} = \lambda f = V$ is the speed of the wave (not the same as the observer's relative velocity v). Since this quantity is Galilean invariant, observers at S and S' should see the same phase for the same point at the same time, meaning that

$$\phi = \frac{2\pi}{\lambda} (x - vt) = \frac{2\pi}{\lambda} (x' + vt - Vt) = \frac{2\pi}{\lambda} x' - (V - v)t',$$

which further simplifies to

$$= \frac{2\pi}{\lambda} x' - \frac{2\pi}{\lambda} V \left(1 - \frac{v}{V} \right) t',$$

should be equal to the phase $\phi' = \frac{2\pi}{\lambda'} x' - \frac{2\pi}{\lambda'} t'$ seen by the moving observer. In particular, the wavenumber and angular frequency satisfy $k' = \frac{2\pi}{\lambda'}$ and $\omega' = \frac{2\pi}{\lambda'} V \left(1 - \frac{v}{V} \right)$, so that

$$\boxed{\omega' = \omega \left(1 - \frac{v}{V} \right), \quad k' = k \implies \lambda' = \lambda}$$

for an ordinary wave moving in a medium. So the takeaway is that our de Broglie matter wave does not behave like an ordinary sound wave – instead, **two observers may observe different values for the wavefunction, meaning Ψ is not directly measurable**. (In fact, we've already seen some hints of this – for example, we mentioned that we can multiply our wavefunction by constants, including phases, and that doesn't change the physical meaning.) Additionally, **wavefunctions are not Galilean invariant**, but (as an exercise left for us) the values of the wavefunction between two observers are still related.

Notice that while we've talked a lot about the wavelengths of the de Broglie waves, we haven't discussed their frequencies yet. de Broglie did in fact answer that as well: since $p = \hbar k$, we'll also set $E = \hbar \omega$, and thus the frequency of a matter wave is $\omega = \frac{E}{\hbar}$, where E is the particle's energy. This is one of the postulates of quantum mechanics, and we'll try to explain why it makes sense now.

Definition 34

The **phase velocity** of a wave with phase $kx - \omega t$ is

$$v_{\text{phase}} = \frac{\omega}{k}.$$

The phase velocity is the velocity with which the nodes and extrema of the wave will move. If we're working

non-relativistically, our de Broglie waves satisfy

$$v_{\text{phase}} = \frac{\omega}{k} = \frac{E}{p} = \frac{\frac{1}{2}mv^2}{mv} = \frac{1}{2}v,$$

and something may seem to be weird because the de Broglie wave looks like it's moving at half the speed of the particle. But that's not unexpected – plane waves themselves don't carry any signal, and instead we should be representing particles with a wave **packet**. So phase velocity is not a very meaningful physical quantity, and instead we should use the following:

Definition 35

The **group velocity** of a wave with phase $kx - \omega t$ is

$$v_{\text{group}} = \left. \frac{d\omega}{dk} \right|_k$$

evaluated at the wavenumber k that we're propagating.

This group velocity, for a de Broglie wave, is then

$$v_{\text{group}} = \left. \frac{d\omega}{dk} \right|_k = \frac{dE}{dp} = \frac{d(p^2/2m)}{dp} = \frac{p}{m} = v,$$

as we expect from a propagating particle.

Fact 36

If we look at the relativistic version of energy and momentum and do all of these calculations again, we'll again find the the group velocity v_{group} lines up with the velocity v of the particle. And in fact, there is some motivation from relativity here – in special relativity, $(\frac{E}{c}, \vec{p})$ form a four-vector, and similarly $(\frac{\omega}{c}, \vec{k})$ also form a four-vector, so it makes sense to set the two four-vectors proportional to each other through this constant \hbar .

(In our equations above, like $p = \hbar k$, we really have vector identities in multiple dimensions and p, k represent the corresponding vector magnitudes.) The above argument, combined with Einstein's claim of $E = h\nu = \hbar\omega$ for photons, provides even more justification for why these de Broglie waves indeed have angular frequency $\frac{E}{\hbar}$.

We'll now return more to our discussion of **group velocity**. There are certain waves where given the wavenumber k , we can write down the corresponding $\omega = \omega(k)$: for example, for light waves we have $\omega = kc$, but for other waves the relation is more complicated (for example, $\omega \propto k^2$ in mechanics, because $E \propto p^2$). Then in general, the group velocity represents the velocity of a **wave packet constructed via superposition**, taking the form

$$\Psi(x, t) = \int \Phi(k) e^{i(kx - \omega(k)t)} dk,$$

where we integrate as a continuous sum, where $e^{i(kx - \omega(k)t)}$ represents a wave at wavenumber k and angular frequency $\omega(k)$, and $\Phi(k)$ is the amplitude of the wave at wavenumber k . Specifically, being able to talk about a group velocity means that we **consider the case where** $\Phi(k)$ is **peaked at some value** k_0 , and we want to see how the superposition moves in time. We can answer that question quickly or more rigorously:

Quick explanation of group velocity. We can use the **principle of stationary phase**, which is essentially just mathematical intuition. If we look at an expression like $f(x) \sin x$, where f is some positive-valued function, we'll have a function which is positive half the time and negative half the time, so it will contribute very little to the integral if f is slowly varying relative to $\sin x$ (because adjacent parts will cancel).

The principle of stationary phase then basically says that integrating something like $f(x) \sin x$ only gives us a contribution when the wave varies slowly (and thus the “phase is stationary”). So in the integral above, we can just integrate from $k_0 - \delta$ to $k_0 + \delta$, since the only place where the peaked $\Phi(k)$ contributes is around $k = k_0$, **and then** we require that Φ is stationary with respect to k . And that means our wavefunction is only significantly nonzero around k_0 if

$$0 = \left. \frac{d\phi(k)}{dk} \right|_{k_0} = x - \left. \frac{d\omega(k)}{dk} \right|_{k_0} t = 0,$$

meaning that $x = \left. \frac{d\omega}{dk} \right|_{k_0} t$ and the group velocity is indeed the speed at which the wave packet is propagating. \square

We'll now actually evaluate the integral and show that the shape of the wave does move with velocity v_{group} :

More rigorous derivation of group velocity. Start with the above equation for the wavefunction

$$\Psi(x, t) = \int \Phi(k) e^{i(kx - \omega(k)t)} dk.$$

Evaluating at $t = 0$, we have

$$\Psi(x, 0) = \int \Phi(k) e^{ikx} dk,$$

which we'll come back to later. Turning back to the original integral, we do a Taylor expansion

$$\omega(k) = \omega(k_0) + (k - k_0) \left. \frac{d\omega}{dk} \right|_{k=k_0} + O((k - k_0)^2),$$

since the values of k that matter are those near k_0 anyway. (And with this we already see the group velocity popping up, which is a good sign.) Splitting up the exponential, we find

$$\Psi(x, t) = \int dk \Phi(k) e^{ikx} e^{-i\omega(k_0)t} e^{-ik \left. \frac{d\omega}{dk} \right|_{k_0} t} e^{ik_0 \left. \frac{d\omega}{dk} \right|_{k_0} t} e^{\text{(negligible)}}$$

(we note here that the negligible term is important if we care about the **distortion** of the wave pattern, which we won't talk about for a few lectures). This integral may look difficult, but the $e^{-i\omega(k_0)t}$ factor can come out, and so can the $e^{ik_0 \left. \frac{d\omega}{dk} \right|_{k=k_0} t}$ factor, meaning that we're left with

$$= e^{-i\omega(k_0)t} e^{ik_0 \left. \frac{d\omega}{dk} \right|_{k_0} t} \int dk \Phi(k) e^{ikx} e^{-ik \left. \frac{d\omega}{dk} \right|_{k_0} t}.$$

But now the first two terms in front of the integral are pure phases, and the integral resembles the wavefunction at $t = 0$ (no $\omega(k)$ factor), so if we take **magnitudes** on both sides, we arrive at

$$\boxed{|\Psi(x, t)| = \left| \Psi \left(x - \left. \frac{d\omega}{dk} \right|_{k_0} t, 0 \right) \right|}.$$

In other words, the norm of the wave at time t looks like the norm of the wave at time 0, but with an additional displacement distance of $v_{\text{group}}t$. So a peak that started at $x = 0$ at $t = 0$ will move to $x = v_{\text{group}}t$ at time t , indeed showing that the shape of the wave packet moves at the group velocity. \square

With all of that discussion done, we're finally ready to write down the equation of a matter wave. If we have a particle of energy E and momentum p , we know that $E = \hbar\omega$ and $p = \hbar k$, and we're going to make an argument based on **superposition and probability** to find the shape of the wave. If we want a plane wave in the $x+$ direction, we might have a wave of the form $\sin(kx - \omega t)$, $\cos(kx - \omega t)$, $e^{ikx - i\omega t}$, or $e^{-ikx + i\omega t}$ (all of these are periodic functions that depend on the phase $kx - \omega t$). But suppose we want a wavefunction of a particle with equal probability of

traveling to the right or to the left. Then using sin requires us to write down a wavefunction like

$$\sin(kx - \omega t) + \sin(kx + \omega t),$$

(since having equal coefficients gives us “equal probability” of moving in each direction), but expanding this gives us

$$= 2 \sin kx \cos \omega t,$$

which is not acceptable because this wavefunction is **identically zero** at $\omega t = \frac{\pi}{2}, \frac{3\pi}{2}, \dots$, meaning that the particle has completely vanished. So that kind of wave (and similarly trying to produce a wavefunction out of cosines, yielding $2 \cos kx \cos \omega t$) won't work for us, and instead we'll want a wavefunction of the form

$$e^{ikx - i\omega t} + e^{-ikx - i\omega t} = 2 \cos kx e^{-i\omega t}.$$

This wavefunction now never vanishes for any value of t , since the t -dependence is always a phase, so there's nothing problematic that occurs here! Similarly, we can also use a $+i\omega t$ in the exponential and write

$$e^{-ikx + i\omega t} + e^{ikx + i\omega t} = 2 \cos kx e^{i\omega t},$$

and again we have not run into trouble yet. But we can't use both of these kinds of matter waves at once – indeed, if both of them were correct, then we could superimpose $e^{ikx - i\omega t}$ and $e^{-ikx + i\omega t}$ (both representing a particle moving to the right), and if both represent the same state then the superposition should also give us a particle moving to the right. But instead, we get

$$e^{ikx - i\omega t} + e^{-ikx + i\omega t} = 2 \cos(kx - \omega t),$$

and we've already seen that we can't have that be a wavefunction that represents a right-moving particle. All of this is to say that we must choose one of the exponentials to be the wavefunction for a de Broglie matter wave, and by convention the following is decided:

Proposition 37 (de Broglie)

The **matter wave** (also **wavefunction**) for a particle with momentum $p = \hbar k$ and energy $E = \hbar \omega$ is

$$\Psi(x, t) = e^{ikx - i\omega t}.$$

(In three dimensions, we replace kx with $\vec{k} \cdot \vec{x}$ and $p = \hbar k$ with $\vec{p} = \hbar \vec{k}$.)

Next lecture, we'll determine the wave equation that this matter wave satisfies, and that will lead us to the Schrodinger equation.

Lecture 5: The Schrodinger Equation

Last time, we discussed de Broglie waves, and we found that we could write down the equations for plane waves corresponding to particles of a particular momentum p and energy E (Proposition 37) – this gives us the **wavefunction for a free particle**. Our goal is to use this particular wavefunction to understand the **equation** governing general potentials (and in particular, we should be able to go from the equation to the wavefunction for a free particle, and then hopefully we can generalize).

Our first task is to understand what kind of (differential) equation this wavefunction will satisfy. First of all, if we have this wavefunction $\Psi(x, t) = e^{ikx - i\omega t}$ and we want to extract the momentum of the particle, then we'll want to

take an x -derivative to get out a factor of k :

$$\frac{\hbar}{i} \frac{\partial}{\partial x} \Psi(x, t) = \hbar k e^{ikx - i\omega t} = p \Psi(x, t).$$

In other words, acting with the differential operator $\frac{\hbar}{i} \frac{\partial}{\partial x} = -i\hbar \frac{\partial}{\partial x}$ on the wavefunction gives us the momentum (a number) times that same wavefunction – thus, remember that operators take in functions and give us back functions, so this is the closest we'll get to extracting a pure quantity out of the wavefunction.

Definition 38

The **momentum operator**, denoted \hat{p} , is the differential operator

$$\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}.$$

For our free particle, we then get the equation $\hat{p}\Psi(x, t) = p\Psi(x, t)$, and when we have an equation of this form (operator on function equals number times function), the function $\Psi(x, t)$ is called an **eigenstate** of the operator \hat{p} with **eigenvalue** p . (This language is motivated by linear algebra, in which we have **eigenvalues** and **eigenvectors** of a matrix M when there are equations of the form $Mv = \lambda v$.) Not all wavefunctions are eigenstates, just like most vectors are not eigenvectors of a given matrix (the matrix will usually rotate the vector in some way), but the eigenstates will be important for us in describing physical characteristics. In particular, what we're saying is that $\Psi(x, t)$ is a **state of definite momentum**: if we measure the momentum of the state, we will always find p (with no uncertainty). And of course, that's what we want, because this is supposed to be the wavefunction of a free particle of momentum p .

We'll now consider another aspect of this wavefunction: since we can extract the momentum p , it makes sense to also extract the energy E of the particle. Notice that (because $\Psi = e^{ikx} e^{-i\omega t}$) taking a time-derivative yields

$$i\hbar \frac{\partial}{\partial t} \Psi = (i\hbar)(-i\omega)\Psi = \hbar\omega\Psi = E\Psi.$$

The result $i\hbar \frac{\partial}{\partial t} \Psi = E\Psi$ is another eigenvalue equation, telling us how a wavefunction of energy E evolves over time.

But this time, we can extract even more physics: remember that for a nonrelativistic particle, we have $E = \frac{p^2}{2m}$, and we want to capture this dependence in some way. Specifically, we'll try to write down **another operator** O satisfying $O\Psi = E\Psi$, and because $E = \frac{p^2}{2m}$ and $p\Psi = \hat{p}\Psi$, we have

$$E\Psi = \frac{p}{2m}(p\Psi) = \frac{p}{2m} \frac{\hbar}{i} \frac{\partial}{\partial x} \Psi$$

(where we've replaced one copy of p with a \hat{p}), and because the other p is still a constant we can move it inside the derivatives and other constants to get

$$= \frac{1}{2m} \frac{\hbar}{i} \frac{\partial}{\partial x} (p\Psi) = \frac{1}{2m} \frac{\hbar}{i} \frac{\partial}{\partial x} \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi,$$

and now setting the first and last expressions equal gives us the equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi = E\Psi,$$

which is another eigenvalue equation and motivates the following definition:

Definition 39

The **energy operator** for a free particle, denoted \hat{E} , is the differential operator

$$\hat{E} = -\frac{\hbar^2}{2m} \frac{\partial}{\partial x^2}.$$

In particular, Ψ is an energy eigenstate (of energy E), or equivalently Ψ is a state of definite energy, and from the way we defined the energy operator we also have $\hat{E} = \frac{1}{2m}\hat{p}^2$. And if we now look at the two eigenvalue equations involving E , we arrive at the equation

$$-\frac{\hbar^2}{2m} \frac{\partial}{\partial x^2} \Psi = i\hbar \frac{\partial}{\partial t} \Psi.$$

This is the **free Schrodinger equation**, and it carries a lot of information. For example, it tells us the relation between k and ω for a de Broglie matter wave, because **trying** the solution $\Psi = e^{ikx - i\omega t}$ gives us

$$i\hbar(-i\omega)\Psi = -\frac{\hbar^2}{2m}(ik)^2\Psi \implies \hbar\omega = \frac{\hbar^2 k^2}{2m} \iff E = \frac{p^2}{2m}.$$

So the differential equation admits plane waves as solutions but constrains the momentum and energy of our particles, and thus we really are making progress towards describing our general wavefunctions. In particular, notice that this free Schrodinger equation is linear, so superpositions of solutions Ψ are also solutions, and **linearity tells us that sums of plane waves are also solutions to the free Schrodinger equation**. Fourier theory then tells us that given plane waves, we can construct whatever wave packet we want, and then we know how to evolve the wavefunction over time because we've already described how to evolve each plane wave over time!

Remark 40. *This kind of logic is common in physics: we take little pieces of evidence and put them together, and even if they don't completely rigorously lead to a given conclusion, we will have good reason to believe the end result (in this case, the Schrodinger equation).*

Rephrasing the paragraph above, our most general solution $\Psi(x, t)$ to the free Schrodinger equation is (integrating over waves of different wavenumbers)

$$\Psi(x, t) = \int_{-\infty}^{\infty} \Phi(k) e^{ikx - i\omega(k)t} dk.$$

As previously discussed, such a wave moves with a group velocity $\left. \frac{d\omega}{dk} \right|_{k_0} = \frac{dE}{dp} = \frac{p}{m} = v$ if $\Phi(k)$ is localized at k_0 (and if it is not localized then the group velocity does not make sense). We can also make a few more observations:

- The "full wavefunction" Ψ cannot be purely real, because the left-hand side of the free Schrodinger equation would then be purely imaginary and the right-hand side would be purely real, but Ψ cannot be identically zero. (Later on, we'll talk about time-independent wavefunctions, and those will be allowed to be purely real.)
- Even though we have a wave moving at some speed v , the free Schrodinger equation is **not** like the usual wave equation $\frac{\partial^2 \Psi}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \Psi}{\partial t^2} = 0$, both because of the number of derivatives and because there is no i in the ordinary wave equation.

Taking another look at the energy operator $\hat{E} = \frac{\hat{p}^2}{2m}$ (which looks like our usual "kinetic energy" in classical mechanics), the next natural step is to add in a **potential** $V(x, t)$, so that our total energy is $E = \frac{p^2}{2m} + V$. It then makes sense to modify our energy operator definition, and there is a different naming convention in this general case:

Definition 41

The **Hamiltonian operator**, denoted \hat{H} , is the differential operator

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x, t).$$

The Hamiltonian basically represents the energy **in terms of** position x and momentum p , and thus we'll need to talk about the position operator as well. But first, this allows us to write down the general Schrodinger equation:

Theorem 42 (Schrodinger equation, one dimension)

The wavefunction Ψ in one dimension satisfies $i\hbar \frac{\partial}{\partial t} \Psi = \hat{H}\Psi$:

$$i\hbar \frac{\partial \Psi}{\partial t} = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t) \right) \Psi.$$

One thing that we may be surprised about is that we multiply our potential V by the wavefunction Ψ , but that's the simplest way that we can keep the differential equation linear – the Hamiltonian must still be a linear operator. In particular, we should think of V not just as a function but also as an operator (which just multiplies a function $f(x, t)$ by $V(x, t)$ to get $f(x, t)V(x, t)$).

Fact 43

Quantum mechanics is about inventing energy operators, solving the resulting Schrodinger equation and finding the valid wavefunctions. In particular, we can consider different potentials V , and the method for solving the resulting Schrodinger equation will vary and give us very different solutions.

As 8.04 goes on, we'll see many of these methods employed, but now that x has showed up we'll spend some time talking about its role in all of this.

Definition 44

The **position operator**, denoted \hat{x} , multiplies functions by x :

$$\hat{x}f(x) = xf(x).$$

The reason we need to be careful with how we write this out is that it illuminates a relation between the position (\hat{x}) and momentum (\hat{p}) operators. One important property of operators (which we may remember from linear algebra in the context of matrices) is that **the order in which they are applied or multiplied matters**. Looking at operators is how Heisenberg arrived at quantum mechanics, and that's discussed more in 8.05, but right now we're interested in looking at whether two operators **commute** (that is, whether the order in which they are applied matters).

Example 45

We determine whether \hat{x} and \hat{p} commute by computing the difference between $\hat{x}\hat{p}\phi$ and $\hat{p}\hat{x}\phi$ (for some function $\phi(x, t)$).

This computation is straightforward, but we need to be careful with it: we wish to evaluate the expression

$$\hat{x}\hat{p}\phi - \hat{p}\hat{x}\phi,$$

but when we write down an expression like $\hat{A}\hat{B}\phi$ for operators \hat{A}, \hat{B} , we really mean $\hat{A}(\hat{B}\phi)$ (because we're first applying \hat{B} to ϕ , and then we apply \hat{A} to that result). Thus, we are evaluating

$$\boxed{\hat{x}(\hat{p}\phi) - \hat{p}(\hat{x}\phi)} = \hat{x} \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \phi \right) - \hat{p}(x\phi),$$

and now both terms in parentheses are functions of x and t , so we can apply the definitions of \hat{x} and \hat{p} again to get

$$= \frac{\hbar}{i} x \frac{\partial}{\partial x} \phi - \frac{\hbar}{i} \frac{\partial}{\partial x} (x\phi).$$

We now use the product rule on the second term, and one of the two parts will cancel with the first term:

$$= \frac{\hbar}{i} x \frac{\partial}{\partial x} \phi - \frac{\hbar}{i} \phi - \frac{\hbar}{i} x \frac{\partial}{\partial x} \phi = \boxed{i\hbar\phi}.$$

Equating the positive parts, and using the fact that $(\hat{A} + \hat{B})\phi = \hat{A}\phi + \hat{B}\phi$, we find that

$$(\hat{x}\hat{p} - \hat{p}\hat{x})\phi = i\hbar\phi$$

for **any** function ϕ , meaning that the operators acting on ϕ must also be identical. We'll use the following notation throughout the rest of the course:

Definition 46

The **commutator** of two operators \hat{A} and \hat{B} , denoted $[\hat{A}, \hat{B}]$, is the operator $\hat{A}\hat{B} - \hat{B}\hat{A}$.

Proposition 47

We have the equality of operators

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

This nonzero commutator really encodes the fact that the two operators interact nontrivially, and that will be the basis of the **uncertainty principle** later on, as well as the **matrix formulation** of quantum mechanics. (Remember that operators, wavefunctions, and eigenstates correspond to matrices, vectors, and eigenvectors, respectively.)

Example 48

A set of famous **matrix** commutators comes from the Pauli matrices (which we'll talk about in 8.05, encoding the spin of spin 1/2 particles)

$$\sigma_1 = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma_2 = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \sigma_3 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}.$$

Specifically, these matrices lead us to the **spin operator** $\vec{S} = \frac{\hbar}{2}\vec{\sigma}$.

We won't talk much more about spin here in 8.04, but we'll compute the matrix commutators: we can verify that

$$\sigma_1\sigma_2 = \begin{bmatrix} i & 0 \\ 0 & -i \end{bmatrix}, \quad \sigma_2\sigma_1 = \begin{bmatrix} -i & 0 \\ 0 & i \end{bmatrix},$$

so that we actually have the relation

$$[\sigma_1, \sigma_2] = 2i\sigma_3.$$

And even though the commutator of Pauli matrices gives us another Pauli matrix, rather than a number like in the $[\hat{x}, \hat{p}] = i\hbar$ case, we're going to see many more complications with the position and momentum operators – it's much harder to understand fully what that commutator means! In particular, in 8.05, we'll talk more about linear algebra and explain how we can write operators like \hat{x} and \hat{p} using matrix representations, but those matrices will need to be infinite-dimensional. (This is a mathematical exercise – there are no two finite-dimensional matrices whose commutator is a multiple of the identity.) So something strange is going on, but we'll still get more familiar with position and momentum and see where it leads us.

We can generalize the one-dimensional Schrodinger equation from Theorem 42 (to avoid focusing on a simple case, and because we actually live in three dimensions): instead of having $\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$, we now have $\hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}$ (for momentum along the x -direction) and similarly $\hat{p}_y = \frac{\hbar}{i} \frac{\partial}{\partial y}$ and $\hat{p}_z = \frac{\hbar}{i} \frac{\partial}{\partial z}$. (This corresponds to the fact that we can write a de Broglie wave as $e^{i\vec{k}\cdot\vec{x}-i\omega t}$, and then we can expand the dot product out across the three components.) To make the notation easier, we will sometimes replace x, y, z with x_1, x_2, x_3 , so that we can just write $p_k = \frac{\hbar}{i} \frac{\partial}{\partial x_k}$ (where k ranges from 1 to 3). Thus, our momentum operator now operates on **vectors**, and we have

$$\hat{\vec{p}} = \frac{\hbar}{i} \nabla.$$

(Indeed, we can check that $\hat{\vec{p}} e^{i\vec{k}\cdot\vec{x}-i\omega t} = \hbar\vec{k} e^{i\vec{k}\cdot\vec{x}-i\omega t}$, and thus we still have a valid eigenvalue equation.) The Schrodinger equation does not become much more complicated, because the Hamiltonian operator is now

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

and the squared vector operator really means that we have

$$(\hat{\vec{p}})^2 = \frac{\hbar}{i} \nabla \cdot \frac{\hbar}{i} \nabla = -\hbar^2 \nabla^2,$$

where ∇^2 is the **Laplacian operator**. This gives us the following general three-dimensional Schrodinger equation:

Theorem 49 (Schrodinger equation, three dimensions)

The wavefunction Ψ in three dimensions satisfies $i\hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi$:

$$i\hbar \frac{\partial \Psi}{\partial t} = \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{x}, t) \right) \Psi.$$

This three-dimensional equation follows pretty naturally from the one-dimensional equation, but we're introducing it now so we keep it in mind throughout all of our work solving differential equations in this class. And the commutation relation $[\hat{x}, \hat{p}] = i\hbar$ now still holds for \hat{x}_k and \hat{p}_k for each k , but operators like \hat{p}_x and \hat{y} **do** commute (because y is a constant with respect to the x -derivative). We can summarize the nine different commutators between position and momentum operators in the concise statement

$$[\hat{x}_i, \hat{p}_j] = i\hbar \delta_{ij},$$

where δ_{ij} is the **Kronecker delta** symbol which returns 1 if $i = j$ and 0 otherwise.

Our final task in this lecture will be to return to the wavefunction and understand its interpretation. We've taken the de Broglie matter wave and used it to obtain a differential equation, but we still don't know what Ψ actually means. Schrodinger initially thought that the spread of the wavefunction (under the Schrodinger equation) represented disintegrating particles, so that more Ψ represents more of the particle. But physicists found that when a particle

comes in and hits a Coulomb potential, the wavefunction falls away as $\frac{1}{r}$, but that is in fact not what happens – experimentally, the particle chooses a direction to go in and stays localized.

So **Born's interpretation of the wavefunction in terms of probability** was the one that made sense – Schrodinger, Einstein, and many others hated it, but over time physicists had to agree that it was right. The statement is essentially that $\Psi(x)$ gives us the **probability (density) of finding the particle at position x at time t** ; more rigorously, this means that if we look at an infinitesimally small box d^3x around a point x , then the probability of finding the particle inside that cube is

$$dP(\vec{x}, t) = |\Psi(x, t)|^2 d^3x.$$

In particular, for this to be a valid probabilistic interpretation, the probability of finding the particle anywhere in space must be 100% (we must measure it to be somewhere), and thus

$$1 = \int_{\mathbb{R}^3} |\Psi(x, t)|^2 d^3x.$$

But already this interpretation adds a few complications. In particular, because the Schrodinger equation tells us how to evolve our wavefunction forward in time, knowing $\Psi(x, t_0)$ for all x allows us to know $\Psi(x, t)$ for all x and all $t > t_0$, thus specifying the wavefunction for all future times. But for the Born interpretation to make sense, we must ensure that as long as the boxed equation holds at some time t_0 , it will still hold at all future times $t > t_0$ (in other words, the **normalization** of our wavefunction preserves probability). We'll do that discussion next time!

Lecture 6: Probability Density, Current, and Conservation

Last time, we described the Schrodinger equation and started discussing the interpretation of the wavefunction. Specifically, we mentioned that in one dimension, $|\Psi(x, t)|^2 dx$ gives us the probability for our particle to be found in an interval of length dx around a particular position x (at some particular time t), and thus if we integrate across all possible values x , we must have $1 = \int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx$ so that the total probability is 1. But for our discussion to be consistent, we need to ensure that this boxed normalization condition will continue to hold at future times if it holds at a particular time t_0 , and that's what we'll verify today. Along the way, we'll understand various important features of wavefunctions and Hamiltonian operators, and we'll also understand the concept of **probability current**.

First, we take another look at the boxed normalization equation – notice that if Ψ approaches some nonzero constant at $\pm\infty$, then the integral will definitely be infinite. Thus, we must impose some boundary conditions: **we require**

$$\lim_{x \rightarrow \pm\infty} \Psi(x, t) = 0.$$

Remark 50. *While there are technically mathematical examples where $\Psi(x, t)$ does not have a limit as $x \rightarrow \infty$, and the integral of $|\Psi|^2$ still converges, those examples do not pop up in any physical contexts and thus we are (mostly) safe to ignore them.*

In addition, we'll require that the function Ψ does not oscillate too quickly: **we also ask that**

$$\frac{\partial \Psi(x, t)}{\partial x} \text{ is bounded as } x \rightarrow \pm\infty.$$

(Since the Schrodinger equation has derivatives in it, we should not be surprised that we need some regularity in Ψ of this form.)

We should now turn back to a statement we made a few lectures ago, in which we stated that Ψ and $c\Psi$ always

represent the same state. Multiplying Ψ by a constant c multiplies the integral $\int_{-\infty}^{\infty} |\Psi|^2$ by a factor of $|c|^2$, so it may seem weird that the normalization condition holds for one but not the other if they're the same state. That can be clarified through the following statement:

Definition 51

For a wavefunction $\Psi(x, t)$ with $\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx$ equal to some finite number N , we say that Ψ is **normalizable**, and we let $\Psi' = \frac{\Psi}{\sqrt{N}}$ be the associated **normalized wavefunction**.

In particular, we have

$$\int_{-\infty}^{\infty} |\Psi'(x, t)|^2 dx = \int_{-\infty}^{\infty} \frac{|\Psi(x, t)|^2}{N} dx = \frac{N}{N} = 1,$$

so Ψ' is indeed normalized and is equivalent to the original wavefunction Ψ . And whenever we work with probabilities and probabilistic statements, we're pre-normalizing our wavefunctions Ψ – in principle, we can always work with normalizable wavefunctions and divide by \sqrt{N} only when needed. But we'll be flexible and do whatever is more convenient for us, because multiplying by a constant does not change whether a wavefunction is normalizable or not.

We're now ready to do the check of **conservation of probability** under the Schrodinger equation. We start with a normalized wavefunction at time t_0 , so that (noting that $|\Psi|^2 = \Psi\Psi^*$)

$$\int \Psi^*(x, t_0)\Psi(x, t_0) dx = 1.$$

Here, we'll let $\Psi^*(x, t_0)\Psi(x, t_0)$ be called the **probability density** (whose interpretation we've already discussed), and we denote it by $\rho(x, t)$. Then we can define $N(t) = \int \rho(x, t) dx$, and our goal is to show that $N(t) = 1$ for all $t > t_0$, given that $N(t_0) = 1$. Rephrasing the question, **we thus wish to show that the Schrodinger equation guarantees $\frac{dN}{dt} = 0$.**

To check this, we write out the definition of N in the derivative: by differentiation under the integral sign and the product rule, we have

$$\frac{dN}{dt} = \int \frac{\partial}{\partial t} \rho(x, t) dx = \int \left(\frac{\partial \Psi^*}{\partial t} \Psi + \Psi^* \frac{\partial \Psi}{\partial t} \right) dx.$$

We now have a time-derivative of Ψ , so here is where we can use the Schrodinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi \iff \frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar} \hat{H}\Psi.$$

But we also have a time-derivative of the complex conjugate Ψ^* , so we want to take a complex conjugate of the equation above, which gives us

$$-i\hbar \left(\frac{\partial \Psi}{\partial t} \right)^* = (\hat{H}\Psi)^* \iff \frac{\partial \Psi^*}{\partial t} = \frac{i}{\hbar} (\hat{H}\Psi)^*,$$

because the complex conjugate of the partial derivative is also the partial derivative of the complex conjugate. Plugging those boxed expressions back into our calculation above yields

$$\frac{dN}{dt} = \int \frac{i}{\hbar} ((\hat{H}\Psi)^* \Psi - \Psi^* (\hat{H}\Psi)) dx,$$

and in order for this to be zero, it's equivalent to ask for the identity

$$\int (\hat{H}\Psi)^* \Psi dx = \int \Psi^* (\hat{H}\Psi) dx$$

to hold, where on one side the conjugate is with the \hat{H} term, and on the other it's not. So conservation of probability has been rephrased into a condition on the Hamiltonian \hat{H} , and it turns out a situation where we do have this condition is when \hat{H} is a **Hermitian** operator. More generally, Hermitian operators should satisfy

$$\int (\hat{H}\Psi_1)^*\Psi_2 = \int \Psi_1^*(\hat{H}\Psi_2)$$

for all wavefunctions Ψ_1, Ψ_2 – applying this to $\Psi_1 = \Psi_2 = \Psi$ gives us $\frac{dN}{dt} = 0$ above. But the actual definition is more general:

Definition 52

For any (linear) operator T , the **Hermitian conjugate** of T , denoted T^* or T^\dagger , is the linear operator that satisfies

$$\int \Psi_1^* T \Psi_2 = \int (T^\dagger \Psi_1)^* \Psi_2.$$

We say that T is **Hermitian** if $T = T^*$.

It's useful to think of Hermitian conjugates as similar to complex conjugates, so that Hermitian operators are similar to real numbers. We'll talk more about this later on, especially in 8.05, but for now we'll get back to the calculation, since we know the actual formula for our Hamiltonian. Plugging in the expression $\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t)$ yields

$$\begin{aligned} \frac{dN}{dt} &= \int \frac{i}{\hbar} ((\hat{H}\Psi)^*\Psi - \Psi^*(\hat{H}\Psi)) dx = \int \frac{i}{\hbar} ((\hat{H}\Psi)^*\Psi - \Psi^*(\hat{H}\Psi)) dx \\ &= \int \frac{i}{\hbar} \left(-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} \Psi + V(x, t) \Psi^* \Psi + \frac{\hbar^2}{2m} \Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \Psi^* V(x, t) \Psi \right) dx, \end{aligned}$$

where we've used the fact that $V(x, t)$ is always real (because it's some energy). Since $V(x, t)$ is just some number, the second and fourth terms in the parentheses cancel out, and we're left with

$$= -\frac{i\hbar}{2m} \int \left(\frac{\partial^2 \Psi^*}{\partial x^2} \Psi - \Psi^* \frac{\partial^2 \Psi}{\partial x^2} \right) dx.$$

This integrand is not zero, but one common way in physics to show that an integral vanishes is to show that the integrand is actually a total derivative (and show that the boundary terms also vanish). Indeed, we can verify directly that

$$\frac{\partial^2 \Psi^*}{\partial x^2} \Psi - \Psi^* \frac{\partial^2 \Psi}{\partial x^2} = \frac{\partial}{\partial x} \left(\frac{\partial \Psi^*}{\partial x} \Psi - \Psi^* \frac{\partial \Psi}{\partial x} \right)$$

by expanding out the product rule and noting that two of the terms cancel out and the other two give us the desired integrand. Plugging back in and rewriting $-\frac{i\hbar}{2m}$ as $\frac{\hbar}{2im}$, we have

$$\frac{dN}{dt} = \int -\frac{\partial}{\partial x} \left[\frac{\hbar}{2im} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x} \right) \right] dx,$$

so the final integral is just the difference of the bracketed term at $x = \infty$ and $x = -\infty$; both of those are zero by our assumptions that Ψ (and therefore Ψ^*) go to 0 at the boundaries, while $\frac{\partial \Psi}{\partial x}$ (and therefore $\frac{\partial \Psi^*}{\partial x}$) are bounded, so both product terms go to 0. This finishes our proof, and we've indeed verified that the wavefunction remains normalizable.

But along the way, we've found something useful for our discussion: notice that inside the total derivative, we have an expression of the form $z - z^*$, where $z = \Psi^* \frac{\partial \Psi}{\partial x}$. Since $z = a + bi \implies z - z^* = (a + bi) - (a - bi) = 2bi = 2i \text{Im}(z)$, what we've actually found is that (reminding ourselves that $\rho(x, t)$ is the probability density)

$$\frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial x} \left[\frac{\hbar}{m} \text{Im} \left(\Psi^* \frac{\partial \Psi}{\partial x} \right) \right].$$

Definition 53

The **current density** $J(x, t)$ for the wavefunction $\Psi(x, t)$ is given by

$$J(x, t) = \frac{\hbar}{m} \operatorname{Im} \left(\Psi^* \frac{\partial \Psi}{\partial x} \right).$$

We can thus rewrite our calculation above in the simpler form

$$\frac{\partial \rho}{\partial t} = -\frac{\partial J}{\partial x} \implies \boxed{\frac{\partial \rho}{\partial t} + \frac{\partial J}{\partial x} = 0},$$

which is a **current conservation statement** similar to what we might have seen in electromagnetism – basically, we begin with a charge density $\rho(x, t)$ (which is really a probability density), and we arrive at a current $J(x, t)$. We'll discuss units briefly here – since $\int |\Psi|^2 = 1$, and we're integrating in one dimension, Ψ has units of $\frac{1}{\sqrt{[L]}}$, and thus

$$\left[\Psi^* \frac{\partial \Psi}{\partial x} \right] = \frac{1}{[L]^2}, \quad [\hbar] = \frac{[M][L]^2}{[T]} \implies \left[\frac{\hbar}{m} \right] = \frac{[L]^2}{[T]},$$

so that our current has units of

$$[J] = \frac{[L]^2}{[T]} \cdot \frac{1}{[L]^2} = \frac{1}{[T]}.$$

This is consistent with what we should expect – probability is unitless, and the probability current gives us a measure of probability (flow) over time.

Remark 54. *This same probability conservation statement can be derived in three dimensions as well, and that's mostly left as an exercise to us. Basically, the three-dimensional current is now vector-valued, involving a divergence:*

$$\vec{J}(x, t) = \frac{\hbar}{m} \operatorname{Im}(\Psi^* \nabla \Psi),$$

so that our current conservation equation becomes

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{J} = 0.$$

This last equation should look familiar to us from 8.02 – it's how Maxwell discovered the displacement current. In this case, we now have $[\vec{J}] = \frac{1}{[L]^2[T]}$ (so the units of current are probability per unit area per unit time).

Returning to our one-dimensional statement

$$\frac{dN}{dt} = \int_{-\infty}^{\infty} \frac{\partial \rho}{\partial t} dx = - \int_{-\infty}^{\infty} \frac{\partial J}{\partial x} dx = -(J(\infty, t) - J(-\infty, t)),$$

where J indeed vanishes at $x \rightarrow \pm\infty$ because of our boundary conditions on the wavefunction Ψ , we've checked that N is conserved and thus our wavefunction stays normalizable (thanks to the existence of a probability current). And because the integral canceled out nicely enough when we used the wavefunction Ψ , it's reasonable to suspect that the Hamiltonian \hat{H} is actually Hermitian (satisfying the equation in Definition 52) – that's an exercise that we can verify ourselves.

We'll finish this lecture by discussing the connection of current conservation to electromagnetism in more detail, which should help clarify some of the intuition. The probability density $\rho(x, t)$ is directly analogous to the charge density, and (integrating that density) the probability to find the particle in some volume is analogous to the charge contained within in some volume. Additionally, the probability current density is just like the current density in electromagnetism.

The key point is that the **existence of a probability current implies local probability conservation**, which is

stronger than just saying that $\frac{dN}{dt} = 0$. Indeed, the differential relation $\frac{\partial \rho}{\partial t} + \frac{\partial J}{\partial x} = 0$ tells us that probability changes somewhere in space are due to some nonzero current at that point, just like a change of charge density is due to some current in electromagnetism.

In particular, the probability that a particle can be found between positions a and b will change only if there is a difference in the currents at the endpoints – let's see this in more detail. If we have some volume V , and we consider the charge in that volume

$$Q_V(t) = \int_V \rho(x, t) d^3x,$$

then we can calculate the change in time of the current via

$$\boxed{\frac{dQ_V(t)}{dt}} = \int_V \frac{\partial \rho}{\partial t} d^3x = - \int_V (\nabla \cdot \vec{J}) d^3x$$

(where we've used current conservation), and now by Gauss's law we can relate the divergence to a surface integral on the boundary S of V ,

$$= \boxed{- \int_S \vec{J} \cdot d\vec{A}}.$$

Indeed, the equality of boxed statements here says that charge is never created or destroyed, so current must escape through the surface in order for the charge inside V to change. And what we're saying here is that **the same holds for probability**: if we look at quantum mechanics in one dimension, and we wish to look at the probability

$$P_{a,b}(t) = \int_a^b \rho(x, t) dx$$

that a particle is found between a and b on the real line, then

$$\boxed{\frac{dP_{a,b}(t)}{dt}} = \int_a^b \frac{\partial \rho(x, t)}{\partial t} dx = - \int_a^b \frac{\partial J}{\partial x} dx = -(J(x=b, t) - J(x=a, t)) = \boxed{J(a, t) - J(b, t)}.$$

In other words, the probability that we find the particle in $[a, b]$ only occurs if probability escapes from the edges: indeed, if a current is positive at a , then probability is moving into the box $[a, b]$ and thus increasing $P_{a,b}$, and if a current is positive at b , then probability is escaping $[a, b]$ and thus decreasing $P_{a,b}$.

Lecture 7: Fourier Transforms, Uncertainty, and Time Evolution

We'll begin today by discussing **wave packets and uncertainty** – this is our first look into the Heisenberg uncertainty relationships, and we'll start by just analyzing our setup at a fixed time $t = 0$. Consider a wavefunction of the form

$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int \Phi(k) e^{ikx} dk$$

which is a superposition of plane waves – in fact, any wavefunction can be written as such a superposition, where the e^{ikx} part represents a wave carrying momentum of $\hbar k$. And we can find the coefficients $\Phi(k)$ if we're given the initial wavefunction $\Psi(x, 0)$, because this discussion falls under the realm of **Fourier analysis**:

Theorem 55 (Fourier inversion)

Suppose $\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int \Phi(k) e^{ikx} dk$. Then we can recover the coefficients via **Fourier inversion**:

$$\Phi(k) = \frac{1}{\sqrt{2\pi}} \int \Psi(x, 0) e^{-ikx} dx.$$

In other words, if we're given an initial wavefunction (like a sine function, or a Gaussian, or a localized wave packet), we can find $\Phi(k)$ by integration, and then we can reconstruct that wavefunction as an integral of plane waves weighted by $\Phi(k)$. We've already talked about a similar idea when discussing group velocity, but for now we'll focus on how to understand uncertainties of position and momentum through this result.

Example 56

As before, consider some $\Phi(k)$ which has a single peak at some wavenumber $k = k_0$, so that it has some **uncertainty** Δk which characterizes the typical width of our peak. Assume that $\Phi(k)$ is real.

We won't make a precise definition of what uncertainty means (that will come later), but for the purpose of intuition, we can imagine taking the **full width at half maximum**, which is the distance between the two points where $\Phi(k)$ achieves half of its peak value. (We don't need to worry about things like factors of 2 from the left and right until future lectures when we're more rigorous.)

Recalling our discussion of stationary phase, we can then also think about the resulting wavefunction $\Psi(x)$; the contribution only comes from around $k = k_0$ because that's the only place where $\Phi(k)$ is large. Furthermore, we need to have a stationary phase at k_0 to have a wave packet, and because $\Phi(k)$ is real it doesn't contribute to the phase, and we just have phase $\phi = kx$ at time $t = 0$ (there is no ωt term). The k -derivative of the phase is then x , meaning that $\Psi(x, 0)$ must be **peaked around $x = 0$** . Thus, we can also associate some uncertainty width Δx to $\Psi(x)$ at time $t = 0$, and we wish to relate Δx and Δk in our subsequent discussion.

Fact 57

We're glossing over a complication here – we claim that $\Psi(x, 0)$ is not real-valued even though $\Phi(k)$ is, so we have to talk about the peak of $|\Psi|(x, 0)$ instead.

Indeed, to check whether Ψ is real, we must compare it to its complex conjugate

$$(\Psi(x, 0))^* = \frac{1}{\sqrt{2\pi}} \int (\Phi(k))^* e^{-ikx} dk$$

(we take the complex conjugate of each term on the right-hand side). We change variables by replacing k with $-k$, which leaves

$$= \frac{1}{\sqrt{2\pi}} \int (\Phi(-k))^* e^{ikx} dk$$

(here dk became $-dk$, but the order of integration switches as well, and those two factors cancel out). Then the **condition for reality of the wavefunction**, meaning that this $\Psi(x, 0)^*$ to be equal to the original $\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int \Phi(k) e^{ikx} dk$, is that

$$\frac{1}{\sqrt{2\pi}} \int (\Phi(k) - \Phi^*(-k)) e^{ikx} dk = 0.$$

For this to hold, it turns out that we must have $\Phi(k) - \Phi^*(-k) = 0$, and the justification for this actually comes from Theorem 55 (because the function $\Phi(k) - \Phi^*(-k)$ has a zero Fourier transform, Fourier inversion tells us that

it must be the zero function). Therefore, we get reality of the wavefunction as long as

$$\boxed{\Phi(k) = \Phi(-k)^*}$$

And indeed, this is not a condition that holds for our wavefunction peaked at some wavenumber $k_0 \neq 0$, so $\Psi(x, 0)$ will not be real in this case.

We're thus ready to return to our discussion of uncertainty and relating Δx and Δk – for this, we write an arbitrary wavenumber as $k = k_0 + \tilde{k}$, so that we have

$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} e^{ik_0x} \int \Phi(k_0 + \tilde{k}) e^{i\tilde{k}x} d\tilde{k},$$

where \tilde{k} is now peaked around 0, and thus the relevant range of integration is in an interval of width on the order of Δk . As we vary \tilde{k} across this width of Δk , the phase in the exponent of $e^{i\tilde{k}x}$ changes by $x\Delta k$ (we can call this the “total phase excursion”). But as long as this phase excursion is small enough – for example, if $\Delta k \cdot x \lesssim 1$ – we'll have a large contribution because the phase doesn't get a chance to wrap around the full 2π . And if $\Delta k \cdot x \gg 1$, then the phase has washed out the contributions of Φ , and thus the wavefunction will turn out to be close to 0. So our final conclusion is basically the following:

$$\Psi(x, 0) \text{ is sizable in an interval } x \in [-x_0, x_0], \text{ where } \Delta k x_0 \lesssim 1.$$

This means that the uncertainty Δx is also roughly on the order of $\frac{1}{\Delta k}$, and overall we have found that $\boxed{\Delta k \Delta x \approx 1}$ for this kind of localized wave packet.

This kind of relation turns out to not be restricted to quantum mechanics – it's only when we start interpreting e^{ikx} as a state of definite momentum that we get the physical connection. Since $p = \hbar k$ for our matter waves, meaning that $\Delta p = \hbar \Delta k$ multiplying both sides of the boxed equation gives us

$$\Delta p \Delta x \approx \hbar.$$

It turns out the more precise result is that $\Delta p \Delta x \geq \frac{\hbar}{2}$ for **any** wavefunction, but we'll need to define uncertainties more rigorously to explain that in full, and we won't do that in this lecture.

Example 58

Consider a $\Phi(k)$ wave which is basically a rectangular pulse:

$$\Phi(k) = \begin{cases} \frac{1}{\sqrt{\Delta k}} & -\frac{\Delta k}{2} < k < \frac{\Delta k}{2}, \\ 0 & \text{otherwise.} \end{cases}$$

Because this function satisfies $\Phi(k) = \Phi(-k)^*$ (the conjugate doesn't matter because Φ is real), the resulting wavefunction will be real; indeed,

$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{-\frac{\Delta k}{2}}^{\frac{\Delta k}{2}} \frac{1}{\sqrt{\Delta k}} dk = \frac{1}{\sqrt{2\pi\Delta k}} \frac{e^{ikx}}{ix} \Big|_{-\frac{\Delta k}{2}}^{\frac{\Delta k}{2}},$$

and after a bit of simplification we arrive at the final answer

$$\boxed{\Psi(x, 0) = \sqrt{\frac{\Delta k}{2\pi}} \frac{\sin\left(\frac{\Delta k x}{2}\right)}{\frac{\Delta k x}{2}}}$$

The typical width of this wavefunction can then be calculated by looking at when it first hits the x -axis, which is at $\pm \frac{2\pi}{\Delta k}$, and thus we find that $\Delta x \approx \frac{2\pi}{\Delta k}$, and indeed $\Delta x \Delta k \approx 2\pi$ regardless of the uncertainty in k .

We'll now move to discussing how our wavepacket evolves, changing shape over time and causing technological complications. Recall that we have

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int \Phi(k) e^{ikx} e^{-i\omega(k)t},$$

and we're still dealing with a wavepacket centered at k_0 , so it still makes sense to expand ω in a Taylor series: this time, we'll write

$$\omega(k) = \omega(k_0) + (k - k_0) \left. \frac{d\omega}{dk} \right|_{k_0} + \frac{1}{2} (k - k_0)^2 \left. \frac{d^2\omega}{dk^2} \right|_{k_0} + \dots,$$

including the second-derivative term. Last time, we only needed the first-derivative term to understand the group velocity, and this time we're going to see how the next term affects the distortion. (Recall that

$$\left. \frac{d\omega}{dk} \right|_{k_0} = \frac{dE}{dp} = \frac{p}{m} = \frac{\hbar k}{m},$$

so taking another derivative should give us

$$\left. \frac{d^2\omega}{dk^2} \right|_{k_0} = \frac{\hbar}{m},$$

and then all future derivatives are zero – the Taylor series actually terminates! Plugging everything back into the integral gives us an additional $e^{-i\frac{1}{2}(k-k_0)^2 \frac{\hbar}{m} t}$ term in the phase, and thus the shape of the wavepacket only significantly changes if this exponent is large. Therefore, roughly **as long as $(k - k_0)^2 \frac{\hbar}{m} |t| \ll 1$, we will see little shape change in our wave packet**. Remembering that $k - k_0$ is on the order of Δk , we're really saying that

$$(\Delta k)^2 \frac{\hbar |t|}{m} \ll 1 \iff \boxed{\frac{(\Delta p)^2 |t|}{\hbar m} \ll 1}.$$

Also using the relation $\Delta p \Delta x \approx \hbar$ from above, we can equivalently phrase this as the condition

$$\boxed{|t| \ll \frac{m}{\hbar} (\Delta x)^2}.$$

In other words, knowing the uncertainty in our particle's momentum or position tells us the amount of time we can wait before the wave starts to significantly distort.

Fact 59

There's yet another way to rewrite these boxed conditions in a more intuitive way, which is

$$\frac{\Delta p |t|}{m} \ll \frac{\hbar}{\Delta p} = \Delta x.$$

This is understandable because it is a statement about lengths: the group velocity is not the same for all of the frequencies, because particles not having a definite momentum means there is some dispersion in the group velocity, corresponding to $\frac{\Delta p}{m}$. And if we multiply that uncertainty by the time $|t|$ that has passed, our shape is only preserved if the distortion is smaller than the uncertainty in the inherent shape of the wavepacket Δx .

Problem 60

If we have a wavepacket of size $\Delta x = 10^{-10}$ m (which is on the order of the size of an atom, so it corresponds to an electron moving around), how long does that packet stay localized?

The answer is that the characteristic timescale here is

$$t \sim \frac{m}{\hbar} (\Delta x)^2 = \frac{mc^2}{\hbar c} \frac{(\Delta x)^2}{c} \approx 10^{-16} \text{ seconds,}$$

and this turns out to be rather important when we think about applications like particle accelerators trying to keep particle bunches together!

With that discussion finished, in the last part of this lecture, we'll finally discuss **time-evolution of a free particle wavepacket**. If we know the shape of an initial wavefunction $\Psi(x, 0)$, and we wish to calculate $\Psi(x, t)$, we first calculate the coefficients

$$\Phi(k) = \frac{1}{\sqrt{2\pi}} \int \Psi(x, 0) e^{-ikx} dx,$$

so that we can rewrite our arbitrary function as a superposition

$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int \Phi(k) e^{ikx} dk,$$

and then we can evolve each of the plane waves in the way that we already know:

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int \Phi(k) e^{i(kx - \omega(k)t)} dk,$$

where we should remember that we have the relation $\hbar\omega(k) = \frac{\hbar^2 k^2}{2m}$ because $E = \frac{p^2}{2m}$. **The key tool that we've used here is linearity**: each plane wave $e^{i(kx - \omega(k)t)}$ solves the Schrodinger equation, so the full integral also does, and we've set up the integral in such a way that it has the correct initial condition at $t = 0$. So this boxed expression is indeed our answer, and if we'd like the solution more explicitly, we can (sometimes) do the k -integral. But the point is that with Fourier inversion, we've found a way to propagate any wavefunction without needing to solve the differential equation directly!

Example 61

If we consider an initial condition which is a Gaussian of uncertainty on the order of a ,

$$\Psi_a(x, 0) = (2\pi)^{-1/4} \frac{1}{\sqrt{a}} \exp\left(-\frac{x^2}{4a^2}\right),$$

we should use the procedure above for time-evolution, finding $\Phi(k)$ and evolving plane waves.

This is an exercise for us – we'll find that Φ is also a Gaussian, the wavefunction spreads out over time, and that the relevant timescale for which this change in width occurs is $\tau = \frac{2ma^2}{\hbar}$.

Lecture 8: Momentum Space and Expectation Values

We'll talk more about momentum space today, understanding its physical relevance and the intimate relation between position and momentum. In particular, we'll try to get to a point where we can think of momentum space as being complementary to the usual coordinate space that we're used to, and that will allow us to discuss expectation values of operators and their time-dependence (which is an important part of quantum dynamics and time-evolution).

We'll begin with a time-independent story, so we suppress the t -dependence in our wavefunction $\Psi(x)$ for simplicity (though everything still works even if we have t). Recall that we had the Fourier decomposition

$$\Psi(x) = \frac{1}{\sqrt{2\pi}} \int \Phi(k) e^{ikx} dk,$$

giving us a similar inverse transform

$$\Phi(k) = \frac{1}{\sqrt{2\pi}} \int \Psi(x) e^{-ikx} dx.$$

In particular, these two equations tell us that knowing $\Phi(k)$ is **equivalent** to knowing $\Psi(x)$, since we can always get from one to the other. Thus, the two representations of the wavefunction carry the same amount of information, and $\Phi(k)$ can be thought of as carrying the weight of the various plane waves in our superposition for $\Psi(x)$. But we can go deeper, and we'll need a technical tool to help us manipulate integrals and functions in our subsequent discussion.

The idea is to try to substitute one of the two equations above into the other, and that will give us the equation for a **delta function**. We have

$$\Psi(x) = \frac{1}{\sqrt{2\pi}} \int \left[\frac{1}{\sqrt{2\pi}} \int \Psi(x') e^{-ikx'} dx' \right] e^{ikx} dk,$$

where we had to be careful when we substituted in the bracketed term for $\Phi(k)$ because x is a dummy variable in that integral and should not be reused. We'll further simplify, changing the order of integration freely (if we want to be more mathematically rigorous we need to be careful with that, but we'll skip the technical details for now), to

$$\Psi(x) = \int_{-\infty}^{\infty} \Psi(x') \frac{1}{2\pi} \int e^{ik(x-x')} dk dx'.$$

The blue term is then a function of the quantity $(x - x')$, and it's what we might recognize as the **delta function** $\delta(x - x')$ (because integrating it against $\Psi(x')$ picks out the integrand at the point where $x' - x = 0$, meaning we are left with $\Psi(x)$). Thus, the integral is one way to represent our delta function, and we note that $\delta(x - x')$ and $\delta(x' - x)$ are equivalent (for example, we can do a change of coordinates in the blue integral $k \mapsto -k$ and preserve everything except the exponent's sign).

Definition 62

The **Dirac delta function** is a "function" given by

$$\delta(x - x') = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ik(x-x')} dk.$$

This delta function is very useful whenever we're dealing with Fourier transforms, but it's a strange integral – notice that when $x = x'$, the integrand is always 1 and the integral diverges, while for nonzero x it's tricky to make the integral converge to any value either. So this expression is singular in a way that forces us to be careful with it, and usually that means that **we will work with the delta function inside integrals**.

Fact 63

If we haven't worked with delta functions before, it's useful to verify using the integral representation that $\delta(ax) = \frac{1}{|a|} \delta(x)$ for any nonzero real number a .

We'll now turn to our discussion about momentum space, starting with the question of **how our normalization condition looks when we switch to $\Phi(k)$ from $\Psi(x)$** . Recall that we start with the normalization condition

$$\int \Psi^*(x) \Psi(x) dx = 1,$$

and we wish to write something similar for $\Phi(k)$; we'll do that by substituting in our Fourier representation of $\Psi(x)$,

using different variables of integration k, k' for the two terms (but the same x):

$$\boxed{\int \Psi^*(x)\Psi(x)dx} = \int \left(\frac{1}{\sqrt{2\pi}} \int \Phi^*(k)e^{-ikx} dk \right) \left(\frac{1}{\sqrt{2\pi}} \int \Phi(k')e^{ik'x} dk' \right) dx.$$

From here, we know that we can't do the integrals over k in general, since those are in the most general form possible, and thus it makes sense to try to do the x -integral. Rewriting the order of the integrals, we have

$$= \int \Phi^*(k) \int \Phi(k') \left(\frac{1}{2\pi} \int e^{i(k'-k)x} dx \right) dk' dk,$$

and now the inner integral is indeed the delta function $\delta(k'-k)$ as in Definition 62, just with different dummy variables, so this simplifies to

$$= \int \Phi^*(k) \int \Phi(k')\delta(k-k')dk' dk = \boxed{\int \Phi^*(k)\Phi(k)dk}.$$

This has actually given us a pretty important mathematical identity:

Theorem 64 (Parseval-Plancherel identity)

For any function $\Psi(x)$ with Fourier transform $\Phi(k)$, we have

$$\int |\Psi(x)|^2 dx = \int |\Phi(k)|^2 dk.$$

In other words, because we get a probabilistic interpretation for the wavefunction when $\int |\Psi(x)|^2 = 1$, **there is also a corresponding probabilistic interpretation for $\Phi(k)$** : we have the same normalization condition $\int |\Phi(k)|^2 = 1$, so it makes sense that we will also have a probability distribution in this “momentum space.”

We've been using k so far instead of $p = \hbar k$, so now we're ready to actually introduce everything in terms of momentum. Since $\frac{dp}{\hbar} = dk$, and we can rewrite functions of k (such as Φ) as functions of p (which we'll respectively denote $\tilde{\Phi}$), and our Fourier relations can now be written in language involving x and p :

$$\Psi(x) = \frac{1}{\sqrt{2\pi}} \int \tilde{\Phi}(p)e^{ipx/\hbar} \frac{dp}{\hbar},$$

$$\tilde{\Phi}(p) = \frac{1}{\sqrt{2\pi}} \int \Psi(x)e^{-ipx/\hbar} dx.$$

We lose a bit of symmetry in our Fourier inversion – there's a factor of \hbar in one equation but not the other, so now we'll define a new function $\Phi(p)$ via $\tilde{\Phi}(p) = \Phi(p)\sqrt{\hbar}$ (where there's some abuse of notation – this $\Phi(p)$ does not have the same functional form as the $\Phi(k)$ above). Checking our constants, we then arrive at the two equations

$$\boxed{\Psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int \Phi(p)e^{ipx/\hbar} dp},$$

$$\boxed{\Phi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int \Psi(x)e^{-ipx/\hbar} dx}.$$

Parseval's theorem also deserves another look: the left-hand side stays the same, and when we convert from $\Phi(k)$ to $\tilde{\Phi}(p)$ we also gain no constant factors, but then we switch to $\Phi(p)$ and pick up a factor of $(\sqrt{\hbar})^2 = \hbar$, canceling out with the $\frac{dp}{\hbar}$ factor when switching integration variables. **So the factors actually cancel out**: Parseval's identity now tells us that

$$\boxed{\int |\Psi(x)|^2 dx = \int |\Phi(p)|^2 dp},$$

and in particular $\Psi(x)$ is normalized if and only if $\Phi(p)$ is.

Fact 65

Much like we did for position, we will thus interpret $|\Phi(p)|^2 dp$ as the probability to find a particle's momentum to be in the range $[p, p + dp]$ (and by conservation of probability and Parseval's theorem, this is indeed valid under time-evolution too).

These equations also have **three-dimensional versions** as well: since we need to do three integrals instead of one, it turns out that we get

$$\Psi(\vec{x}) = \frac{1}{(2\pi\hbar)^{3/2}} \int \Phi(\vec{p}) e^{i\vec{p}\cdot\vec{x}/\hbar} d^3\vec{p},$$

$$\Phi(\vec{p}) = \frac{1}{(2\pi\hbar)^{3/2}} \int \Psi(\vec{x}) e^{-i\vec{p}\cdot\vec{x}/\hbar} d^3\vec{x}.$$

We also similarly have a three-dimensional delta function, also defined with an integral:

$$\delta^3(\vec{x} - \vec{x}') = \frac{1}{(2\pi)^3} \int e^{i\vec{k}\cdot(\vec{x}-\vec{x}')} d^3\vec{k},$$

and Parseval's identity still gives us

$$\int |\Psi(\vec{x})|^2 d^3\vec{x} = \int |\Phi(\vec{p})|^2 d^3\vec{p}.$$

Basically, everything is very analogous in three dimensions and we don't have to memorize anything new!

With that, we're finally ready to discuss **expectation values of operators**, which is one of the first steps towards a **full interpretation** of quantum mechanics. We'll start with the basic probabilistic definition:

Definition 66

Let Q be a random variable which can take values in a finite set $\{Q_1, \dots, Q_n\}$ with probabilities p_1, \dots, p_n , respectively. Then Q has **expectation** or **expected value**

$$\langle Q \rangle = \sum_{i=1}^n p_i Q_i.$$

This is basically a weighted average which tells us the average value obtained by repeatedly taking many samples of Q . Expectations can also be computed for continuous random variables, which is what we need in quantum mechanics for our wavefunction: essentially, because $\Psi^*(x, t)\Psi(x, t)dx$ tells us the probability that our particle is in the range $[x, x + dx]$, we can define the expectation value of \hat{x} , the position operator, via

$$\langle \hat{x} \rangle = \int x \Psi^*(x, t)\Psi(x, t)dx$$

(where x is the value of the position operator, and $\Psi^*(x, t)\Psi(x, t)dx$ is the corresponding probability). What we're really doing here is treating our position operator as a random variable, and experimentally we're saying the following: suppose we have a system that is represented by the wavefunction Ψ . Then if we build many identical copies of this system and measure the positions of the particles (at the same time), then the average value should be close to $\langle \hat{x} \rangle$. The key point to always keep in mind is that repeated measurements of the state can result in varying answers!

Similarly, because we have a probability density for the momentum p (specifically, $|\Phi(p)|^2 dp$ is the probability to find the particle's momentum in $[p, p + dp]$), we should define

$$\langle \hat{p} \rangle = \int p |\Phi(p)|^2 dp.$$

But we know how $\Phi(p)$ is related to $\Psi(x)$ through the Fourier relations, and it's natural to see the expectation value for the momentum operator in terms of the same density as the expectation value for the position operator. So we'll substitute:

$$= \int p \Phi^*(p) \Phi(p) dp,$$

and now writing Φ^* and Φ as integrals over x' and x , respectively, we get

$$= \int_{-\infty}^{\infty} p \left(\int \frac{1}{\sqrt{2\pi\hbar}} e^{ipx'/\hbar} \Psi^*(x') dx' \right) \left(\int \frac{1}{\sqrt{2\pi\hbar}} e^{-ipx/\hbar} \Psi(x) dx \right) dp.$$

Like before, our strategy is to do the p -integral because the others were just written out generically: cleaning up the terms gives us

$$= \frac{1}{2\pi\hbar} \int \Psi^*(x') \int \Psi(x) \left(\int p e^{ipx'/\hbar} e^{-ipx/\hbar} dp \right) dx dx',$$

and now the insight that we should bring in is that "we know the momentum operator is secretly supposed to be $\frac{d}{dx}$." Notice that we can rewrite the **inner** integral as

$$\int p e^{ipx'/\hbar} e^{-ipx/\hbar} dp = \int \left(-\frac{\hbar}{i} \frac{\partial}{\partial x} \right) e^{ipx'/\hbar} e^{-ipx/\hbar} dp,$$

since the x -partial derivative doesn't act on the term with the x' exponent. So now we can move this $-\frac{\hbar}{i} \frac{\partial}{\partial x}$ term out of the innermost integral, since it doesn't have to do with p : a bit more cleaning gives us

$$\langle \hat{p} \rangle = \int \Psi^*(x') \int \Psi(x) \left(-\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \left(\int \frac{1}{2\pi\hbar} e^{ip(x'-x)/\hbar} dp \right) dx dx'.$$

We're almost there – the inner integral is now the delta function $\delta(x - x')$ (if we just do a change of variables $u = \frac{p}{\hbar}$), and then we can do integration by parts on the x -integral to have the $\frac{\partial}{\partial x}$ act on the other term instead. Here, we're using the important theme that while integration by parts has boundary terms, they will vanish as long as our wavefunction goes to 0 sufficiently fast (which we will always assume). Thus, we end up with

$$= \int \Psi^*(x') \int \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi(x) \delta(x - x') dx dx',$$

which we can more clearly write out as

$$= \int \frac{\hbar}{i} \frac{\partial \Psi}{\partial x} \int \Psi^*(x') \delta(x - x') dx' dx.$$

The integral over x' will evaluate $\Psi^*(x')$ at x , so putting everything back together gives us

$$\langle \hat{p} \rangle = \int \frac{\hbar}{i} \Psi^*(x) \frac{\partial \Psi}{\partial x} dx,$$

or in the most revealing form possible, we actually have

$$\boxed{\langle \hat{p} \rangle = \int \Psi^*(x) \hat{p} \Psi(x) dx},$$

where $\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$ is our momentum operator. So even though the expectation value is initially defined by a probabilistic interpretation $\int p |\Phi(p, t)|^2 dp$, the end result is that we sandwich \hat{p} between Ψ^* and Ψ (and only have it act on Ψ). Notice that if we replace the x in the integral for $\langle \hat{x} \rangle$ with an \hat{x} operator between Ψ^* and Ψ , that also gives us the same answer, and this motivates the following general definition:

Definition 67

The expectation value of a quantum mechanical operator \hat{Q} in a state Ψ is defined as

$$\langle \hat{Q} \rangle_{\Psi} = \int \Psi^*(x, t) (\hat{Q} \Psi(x, t)) dx.$$

(If it is clear which state we are referring to, or if we are speaking generically, we will sometimes omit the Ψ subscript for clarity.) Such expectation values are varying in time, and that time-dependence can be studied.

Example 68

Consider the **kinetic operator** $\hat{T} = \frac{\hat{p}^2}{2m}$ – we'll write down its expectation value in the position-space representation.

If we're acting on the wavefunction $\Psi(x)$, then we should think of \hat{p} as $\frac{\hbar}{i} \frac{\partial}{\partial x}$, and thus we have

$$\langle \hat{T} \rangle = \int \Psi^*(x, t) \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x, t) \right) dx.$$

But we can also write down the expectation integral in momentum space, and then \hat{p} acts as p on a wavefunction $\Phi(p)$. Thus, we have

$$\langle \hat{T} \rangle = \int \frac{p^2}{2m} |\Phi(p)|^2 dp = \int \Phi^*(p) \frac{p^2}{2m} \Phi(p) dp,$$

where the first form of the integral comes from the probabilistic definition of expectation values, while the second is thinking of it as a "sandwiched" operator. It might seem like the momentum integral is nicer (in particular, it's manifestly positive because the integrand is positive), but we can actually partially integrate by parts the x -integral to find that we also have

$$\langle \hat{T} \rangle = \int \frac{\hbar^2}{2m} \left| \frac{\partial \Psi}{\partial x} \right|^2 dx,$$

which is also clearly positive. So both integrals are valid to work with!

We can now return to the time-dependence of expectation values, which is a pretty fundamental result in quantum mechanics. We aim to calculate

$$\frac{d}{dt} \langle \hat{Q} \rangle = \frac{d}{dt} \left(\int \Psi^*(x, t) (\hat{Q} \Psi(x, t)) dx \right),$$

and by the product rule this simplifies to

$$= \int \left(\frac{\partial \Psi^*}{\partial t} \hat{Q} \Psi + \Psi^* \hat{Q} \frac{\partial \Psi}{\partial t} \right) dx.$$

But now applying the Schrodinger equation (because that's how we deal with time-derivatives) in the form $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$, we have

$$= \int \left(\frac{i}{\hbar} (\hat{H} \Psi)^* \hat{Q} \Psi - \frac{i}{\hbar} \Psi^* \hat{Q} \hat{H} \Psi \right) dx.$$

Multiplying by $i\hbar$ to cancel out the constants on the right, we now have

$$i\hbar \frac{d}{dt} \langle \hat{Q} \rangle = \int (\Psi^* \hat{Q} \hat{H} \Psi - (\hat{H} \Psi)^* \hat{Q} \Psi) dx,$$

and **by Hermiticity** the \hat{H} on the second term can be brought to act on the other term, $\hat{Q} \Psi$, instead:

$$= \int (\Psi^* \hat{Q} \hat{H} \Psi - \Psi^* \hat{H} \hat{Q} \Psi) dx = \int \Psi^* (\hat{Q} \hat{H} - \hat{H} \hat{Q}) \Psi dx.$$

But now we see a commutator show up – in fact, this is one of the reasons commutators are so important in quantum

physics – and we get the final equation

$$i\hbar \frac{d}{dt} \langle Q \rangle = \int \Psi^* [\hat{Q}, \hat{H}] \Psi dx = \langle [\hat{Q}, \hat{H}] \rangle,$$

where in the last step we've noticed that the commutator sandwiches Ψ^* and Ψ and thus gives us the usual formula for an expectation value. One way to phrase what's happening is that we've actually encoded all of the dynamics in the observables – instead of having wavefunctions changing in time and therefore having expectations change as a result, we have the expectations evolving in terms of their commutators with the Hamiltonian. In particular, any operator expectation that commutes with the Hamiltonian has time-derivative zero, and thus **commutation relations give rise to conservation laws**. For example, since \hat{p} commutes with $\hat{H} = \frac{\hat{p}^2}{2m}$ for the free particle, a free particle's expected momentum must be conserved. We'll see much more of this concept in the future!

Lecture 9: Hermitian Operators, Measurement, and Uncertainty

We'll begin today with the discussion of Hermitian operators as they relate to **physical observables**. Recall that an operator \hat{Q} is **Hermitian** if it satisfies the equation

$$\int \Psi_1^* \hat{Q} \Psi_2 dx = \int (\hat{Q} \Psi_1)^* \Psi_2$$

for any two sufficiently well-behaved wavefunctions Ψ_1, Ψ_2 . We'll sometimes use a more concise notation for these kinds of expressions:

Definition 69

Define the **inner product** (\cdot, \cdot) , which takes in two wavefunctions Ψ_1, Ψ_2 and outputs

$$(\Psi_1, \Psi_2) = \int \Psi_1^*(x) \Psi_2(x) dx.$$

This inner product satisfies some important properties: for example, we can directly check that

$$(a\Psi_1, \Psi_2) = a^*(\Psi_1, \Psi_2), \quad (\Psi_1, a\Psi_2) = a(\Psi_1, \Psi_2).$$

Notice that we can rewrite the definition of Hermiticity in a nicer form now: we are asking for

$$(\Psi_1, \hat{Q}\Psi_2) = (\hat{Q}\Psi_1, \Psi_2)$$

for any two well-behaved wavefunctions Ψ_1, Ψ_2 .

Last time, we also defined the expectation value of the operator \hat{Q} in a state Ψ , given by

$$\langle \hat{Q} \rangle_\Psi = \int \Psi^* \hat{Q} \Psi dx = (\Psi, \hat{Q}\Psi).$$

We'll connect these two ideas together by making a few observations:

Proposition 70

For any Hermitian operator \hat{Q} , the expectation value $\langle \hat{Q} \rangle_\Psi$ is real.

Proof. Notice that

$$(\langle \hat{Q} \rangle_\Psi)^* = \int (\Psi^* \hat{Q} \Psi)^* dx$$

(if we want to take the complex conjugate of an integral, we can just conjugate the integrand). The integrand is the product of Ψ^* and $\hat{Q}\Psi$, which are each complex-valued (**an important note here**: we are not thinking of just conjugating \hat{Q} on its own, because it is acting **on** a wavefunction), and thus we can rewrite this as

$$= \int \Psi(\hat{Q}\Psi)^* dx = \int (\hat{Q}\Psi)^* \Psi dx.$$

where we've used the fact that $(\Psi^*)^* = \Psi$. And now we use the Hermiticity of \hat{Q} to move the \hat{Q} from one term to the other:

$$= \int \Psi^*(\hat{Q}\Psi) dx = \langle \hat{Q} \rangle_{\Psi}.$$

Thus, the expectation value of \hat{Q} is its own conjugate, meaning that it is real. □

Proposition 71

The eigenvalues of a Hermitian operator $\langle \hat{Q} \rangle$ are always real.

(Recall that if we have a wavefunction Ψ_1 that satisfies $\hat{Q}\Psi_1 = q_1\Psi_1$, then q_1 is an **eigenvalue** of \hat{Q} and Ψ_1 is the associated **eigenvector** or **eigenfunction**.)

Proof. Let q_1 be an eigenvalue of \hat{Q} with associated eigenvector Ψ_1 . There are many ways to show this result, but we'll apply Proposition 70 to \hat{Q} in the state Ψ_1 . Then we have the **real number**

$$\langle \hat{Q} \rangle_{\Psi_1} = \int \Psi_1^* \hat{Q} \Psi_1 dx = \int \Psi_1^* q_1 \Psi_1 dx$$

(by the eigenvalue condition), and then taking q_1 out of the integral gives us

$$= q_1 \int \Psi_1^* \Psi_1 dx.$$

The integrand of this integral is always a positive real number, so the integral is real. Because our left-hand side $\langle \hat{Q} \rangle_{\Psi_1}$ was also real, our eigenvalue q_1 is indeed real.

We may notice that Ψ_1 can be arbitrarily scaled and it will still be a valid eigenvector; thus, we can always scale so that “being in the state Ψ_1 ” means that we have a **normalized** state. (In fact, **we must do this normalization** whenever calculating expectation values of our states!) Then the calculation above simplifies to $\langle \hat{Q} \rangle_{\Psi_1} = q_1$, so the **eigenvalue of an operator in a state Ψ_1 is the expectation value of \hat{Q} in that state**, and it is always real (as desired). □

The key point now is that (informally) **Hermitian operators are rich**: they have as many eigenvectors as we need to span the whole space of states. In other words, if we take any Hermitian operator and write down its set of eigenstates, then any wavefunction is a superposition of those eigenstates! (In linear algebra terms, we can think about a finite-dimensional matrix for a Hermitian matrix – what we're saying is that the eigenvectors form a **basis** of the vector space on which the matrix acts on.) This is called the **spectral theorem**, and we'll talk about it more in 8.05 when we have more discussion of linear algebra, but we'll still write out our claim more explicitly.

Proposition 72

For any Hermitian operator \hat{Q} , consider its eigenvalues and eigenfunctions given by

$$\hat{Q}\Psi_1 = q_1\Psi_1, \quad \hat{Q}\Psi_2 = q_2\Psi_2, \dots$$

(the set of which can be finite or infinite). Then the eigenfunctions can be organized to satisfy the **orthonormality** relation

$$\int \Psi_i^*(x)\Psi_j(x)dx = \delta_{ij}$$

In particular, setting $i = j$ tells us that each Ψ_i is a normalized state, so they are “good eigenvectors” in the expectation value sense. But in addition, for any $i \neq j$, we have $(\Psi_i, \Psi_j) = 0$, and we can think of the usual three basis vectors of \mathbb{R}^3 (the x -, y -, and z -direction unit vectors, all of which have unit length and are orthogonal) as an illustrative example of what’s going on more generally! So the inner product we’ve defined should be thought of as a dot product of wavefunctions.

Proof of a simple case. We’ll consider the case where the eigenvalues of different eigenvectors are always different (meaning that $q_i \neq q_j$ if $i \neq j$). In this case, we can always first normalize our eigenfunctions by rescaling. Then we have

$$\int \Psi_i^* \hat{Q} \Psi_j dx = \int \Psi_i^* q_j \Psi_j dx = \boxed{q_j \int \Psi_i^* \Psi_j},$$

but also by Hermiticity we have

$$\int \Psi_i^* \hat{Q} \Psi_j dx = \int (\hat{Q} \Psi_i)^* \Psi_j dx = \int (q_i \Psi_i)^* \Psi_j = \boxed{q_i \int \Psi_i^* \Psi_j},$$

where we know that $q_i^* = q_i$ by Proposition 71. Equating the two boxed expressions, because $q_i \neq q_j$, we must have $\int \Psi_i^* \Psi_j = 0$, as desired. \square

However, the more general case occurs when we have **degeneracy**, and this is a very important concept that often comes up in quantum mechanics. Degeneracy occurs when **several different eigenfunctions have the same eigenvalue** (we’ll in fact see a case where this happens later in the lecture), and in such a case it is important that Proposition 72 includes the clause “can be organized” – we need to pick appropriate eigenfunctions in the eigenspaces, forming linear combinations, so that we do indeed still have orthonormality, and we still do have enough eigenstates to span the whole space. Let’s state that last claim more explicitly:

Proposition 73

The eigenfunctions of any Hermitian operator \hat{Q} form a set of **basis functions**, meaning that any (reasonable) wavefunction Ψ can be written as a superposition

$$\Psi = \alpha_1\Psi_1 + \alpha_2\Psi_2 + \dots = \sum_i \alpha_i\Psi_i.$$

While those coefficients α_i may seem mysterious, we can in fact use Proposition 72 to calculate them easily: we have

$$\boxed{(\Psi_i, \Psi)} = \int \Psi_i^* \sum_j \alpha_j \Psi_j dx$$

(we should make sure not to reuse indices here, which is why we sum over j), and now we can switch the sum and integral to get

$$= \sum_j \alpha_j \int \Psi_i^* \Psi_j dx.$$

But orthonormality tells us that the only term that survives is $i = j$:

$$= \sum_j \alpha_j \delta_{ij} = \boxed{\alpha_i}.$$

Thus, we compute the coefficient α_i (and thus how much of the wavefunction Ψ is “along” the state Ψ_i) by integrating $\Psi_i^* \Psi$. Additionally, we can compute through expansion that

$$\boxed{1} = \int |\Psi|^2 dx = \int \Psi^* \Psi dx = \int \left(\sum_i \alpha_i \Psi_i \right)^* \sum_j \alpha_j \Psi_j dx,$$

and now moving the sum over i, j out, we get

$$\sum_i \sum_j \alpha_i^* \alpha_j \int \Psi_i^* \Psi_j dx = \sum_i \sum_j \alpha_i^* \alpha_j \delta_{ij} = \sum_i \alpha_i^* \alpha_i = \boxed{\sum_i |\alpha_i|^2}.$$

Phrasing this in words, **if we have a state which is a superposition of orthonormal basis vectors, then the sums of squares of coefficients gives us the normalization condition** – there’s no mixing between Ψ_i and Ψ_j . And this expansion can be done for any state and any Hermitian operator!

With that, we’ve done all of the work necessary for stating the **measurement postulate** which we introduced in our beginning lectures:

Theorem 74 (Measurement postulate)

Suppose we measure a Hermitian operator \hat{Q} in a state Ψ . Then the possible results that we may obtain are the eigenvalues q_1, q_2, \dots , and the probability of measuring q_i is

$$p_i = |\alpha_i|^2 = |(\Psi_i, \Psi)|^2.$$

If the outcome of the measurement is q_i , then the state of the system **becomes** Ψ_i (this is called the **collapse** of the wavefunction).

For example, if we measure the kinetic energy of a particle, then we’ll get some eigenvalue of the kinetic operator, and after we measure we’ll be in a state of definite kinetic energy (so that subsequent measurements also give us that same kinetic energy). The key is that this result essentially came from Hermitian operators being rich enough for their eigenvectors to span our space of wavefunctions – if we want to measure some quantity X , we should write our state as a superposition of states with definite X , use the spectral theorem, and then compute the coefficient α_i that is relevant.

This measurement postulate may seem strange to us, because it essentially divides quantum mechanics into two realms: that of the Schrodinger equation (the natural time-evolution) and that of measurement (the collapse). People have wondered why measurement doesn’t come out of the Schrodinger equation if it’s supposed to govern quantum mechanics, but nothing is sufficiently clear for us to question this framing for now, and thus **we’ll take this measurement postulate as an additional assumption of quantum mechanics**.

Example 75

Suppose that we have a state $\Psi = \sum_i \alpha_i \Psi_i$. We'll compute the expectation of \hat{Q} on Ψ in terms of the eigenvectors as a consistency check.

First of all, we have (as we've done before)

$$\langle \hat{Q} \rangle_\Psi = \int \Psi^* \hat{Q} \Psi = \int \left(\sum_i \alpha_i \Psi_i \right)^* \hat{Q} \left(\sum_j \alpha_j \Psi_j \right) dx = \sum_i \sum_j \alpha_i^* \alpha_j \int \Psi_i^* \hat{Q} \Psi_j dx,$$

and now using the eigenvector equations and orthonormality yields

$$= \sum_i \sum_j \alpha_i^* \alpha_j \int \Psi_i^* q_j \Psi_j dx = \sum_i \sum_j \alpha_i^* \alpha_j q_j \delta_{ij} = \boxed{\sum_i |\alpha_i|^2 q_i}.$$

But we've derived this expected result (achieving q_i with probability $|\alpha_i|^2$) with properties of our eigenvectors, **rather than** with the definition of an expectation value of a random variable (which is what the end result here is telling us)! Since the measurement postulate tells us that $p_i = |\alpha_i|^2$, everything we've said so far is consistent. Let's do a physical example to see this in exactation:

Example 76

Consider a free particle on a (topological) circle $x \in [0, L]$, where we identify the points at $x = 0$ and L , and consider the wavefunction at some fixed time

$$\Psi(x) = \sqrt{\frac{2}{L}} \left(\frac{1}{\sqrt{3}} \sin \frac{2\pi x}{L} + \sqrt{\frac{2}{3}} \cos \frac{6\pi x}{L} \right).$$

We'll calculate the **different values and probabilities** that we can obtain when we **measure the momentum** of the particle.

Remark 77. We can verify that $\Psi(L) = \Psi(0)$, so this is a valid wavefunction on the circle. Notice that $\Psi(x)$ is purely real at this point in time, and this is in fact allowed, but our discussion that wavefunctions cannot be purely real (from a previous lecture) tells us that it will not be real forever.

Since we're trying to measure the momentum of our particle, we have to look at the momentum eigenstates, which are plane waves of the form e^{ikx} . On the real line, we could never normalize these states (because the norm squared of e^{ikx} is 1), but on a circle we're actually okay, because there's only a finite length we have to integrate along. Specifically, momentum eigenstates take the form

$$\Psi_m \propto e^{2\pi i m x / L}$$

for some integer m , because these are plane waves that are periodic with period L (meaning that $\Psi(x + L) = \Psi(x)$), so they have definite momentum and we just have to normalize them. For that, notice that the squared norm of $e^{2\pi i m x / L}$ is always 1, so to make the integral 1 over the length L we want

$$\boxed{\Psi_m = \frac{1}{\sqrt{L}} e^{2\pi i m x / L}},$$

for any integer m , to be our normalized momentum eigenstates with corresponding momentum

$$p_m \Psi_m = \frac{\hbar}{i} \frac{\partial}{\partial x} \Psi_m = \frac{2\pi\hbar m}{L} \Psi_m \implies \boxed{p_m = \frac{2\pi\hbar m}{L}}$$

Thus, we've found the momentum eigenfunctions, and all that's left to do is to rewrite our Ψ as a linear combination of the Ψ_m s. The momenta of the different eigenfunctions are all different, so we have orthonormal eigenfunctions and we can just use the trigonometric identities

$$\sin x = \frac{e^{ix} - e^{-ix}}{2i}, \quad \cos x = \frac{e^{ix} + e^{-ix}}{2}$$

from here to find that

$$\Psi = \sqrt{\frac{2}{3}} \frac{1}{2i} \Psi_1 - \sqrt{\frac{2}{3}} \frac{1}{2i} \Psi_{-1} + \frac{1}{\sqrt{3}} \Psi_3 + \frac{1}{\sqrt{3}} \Psi_{-3}.$$

We can now read off the probabilities and measured momenta: since Ψ_m has momentum $\frac{2\pi\hbar m}{L}$, our state Ψ will have momentum $\frac{2\pi\hbar}{L}$ with probability $\left| \sqrt{\frac{2}{3}} \frac{1}{2i} \right|^2 = \frac{1}{6}$, and similarly we'll get momentum $-\frac{2\pi\hbar}{L}$ with probability $\frac{1}{6}$, momentum $\frac{6\pi\hbar}{L}$ with probability $\frac{1}{3}$, and momentum $-\frac{6\pi\hbar}{L}$ with probability $\frac{1}{3}$, when measuring in the state Ψ . These probabilities indeed add to 1, and thus we've now seen an example of decomposition along eigenstates that we've talked about abstractly above.

Finally, in the same probabilistic framework, we can now properly define what **uncertainty** really means in a mathematical context.

Definition 78

Let Q be a random variable which takes on values Q_1, \dots, Q_n with probabilities p_1, \dots, p_n , and suppose its expectation value is $\bar{Q} = \langle Q \rangle = \sum_i p_i Q_i$ (we use \bar{Q} and $\langle Q \rangle$ interchangeably). Then the **variance** of Q is

$$(\Delta Q)^2 = \sum_i p_i (Q_i - \bar{Q})^2,$$

and the **uncertainty** or **standard deviation** of Q is $\Delta Q = \sqrt{(\Delta Q)^2}$.

In other words, the variance calculates the expected (weighted) **squared deviation** from the average – we can indeed see that the right-hand side is always positive because it's a sum of positive terms, so ΔQ will be real. Furthermore, if $\Delta Q = 0$, then each term on the right-hand side must be zero, meaning that $Q_i = \bar{Q}$ for any potential value Q takes on (and thus Q is with probability one just its average value \bar{Q}).

We can simplify the variance with some algebraic manipulation: by expanding, we find that

$$\boxed{(\Delta Q)^2} = \sum_i p_i (Q_i - \bar{Q})^2 = \sum_i p_i Q_i^2 - 2 \sum_i p_i Q_i \bar{Q} + \sum_i p_i \bar{Q}^2.$$

Now we can separate out the different interpretations, noting that \bar{Q} is a constant, and we find that this simplifies to

$$= \bar{Q}^2 - 2\bar{Q} \sum_i p_i Q_i + \bar{Q}^2 \sum_i p_i = \bar{Q}^2 - 2\bar{Q}\bar{Q} + \bar{Q}^2 = \boxed{\bar{Q}^2 - \bar{Q}^2}.$$

In particular, because the variance of a random variable is always nonnegative, we find that $\bar{Q}^2 \geq \bar{Q}^2$ for any real-valued random variable Q . And now this allows us to turn back to the quantum mechanical interpretation:

Definition 79

Let \hat{Q} be a Hermitian operator. We define the **uncertainty of \hat{Q} in the state Ψ** , denoted $(\Delta\hat{Q})_{\Psi}^2$, to be

$$(\Delta\hat{Q})_{\Psi}^2 = \langle Q^2 \rangle_{\Psi} - \langle \hat{Q} \rangle_{\Psi}^2.$$

The point here is that \hat{Q} and \hat{Q}^2 are Hermitian operators, so we can calculate the right-hand side because we always know how to compute expectation values. And from here, we claim the following (which we'll prove next lecture):

Lemma 80

We may write the uncertainty of \hat{Q} in the state Ψ as a single expectation

$$(\Delta\hat{Q})_{\Psi}^2 = \langle (\hat{Q} - \langle \hat{Q} \rangle)^2 \rangle_{\Psi},$$

and we can also write it as an integral

$$(\Delta\hat{Q})_{\Psi}^2 = \int |(Q - \langle Q \rangle)\Psi|^2 dx.$$

(In the above, $\langle Q \rangle$ is the multiplication-by-a-constant operator.) In addition, we'll show that analogous to the zero-variance observation in the probabilistic context, a state Ψ has zero uncertainty for \hat{Q} if and only if it is an eigenstate for \hat{Q} .

Lecture 10: Stationary States and the Particle on a Circle

We'll begin today by analyzing the uncertainty of a Hermitian operator in more detail. Last time, we defined $(\Delta\hat{Q})_{\Psi}^2$ for a Hermitian operator \hat{Q} measured in a state Ψ , and today we'll start by proving the two claims in Lemma 80 from last lecture.

Proof of Lemma 80. For the first claim, we do a direct computation (remembering that $\langle \hat{Q} \rangle$ is thought of as the operator which multiplies any state by the constant $\langle \hat{Q} \rangle$). We expand the square, noticing that $\langle \hat{Q} \rangle$ and \hat{Q} commute (because the former is a number)

$$\langle (\hat{Q} - \langle \hat{Q} \rangle)^2 \rangle = \langle \hat{Q}^2 - 2\langle Q \rangle\hat{Q} + \langle \hat{Q} \rangle^2 \rangle.$$

(Notice that $(A + B)^2 = A^2 + AB + BA + B^2 \neq A^2 + 2AB + B^2$ if A and B don't commute.) Now the expectation of a sum is the sum of the individual expectations, so we can further simplify to

$$= \langle \hat{Q}^2 \rangle - 2\langle \hat{Q} \rangle\langle \hat{Q} \rangle + \langle \hat{Q} \rangle^2$$

(where we've used the fact that we can take constants out of expectations: $\langle c\hat{Q} \rangle = c\langle \hat{Q} \rangle$). Combining the last two terms indeed gives us the definition of the uncertainty of \hat{Q} , as desired.

For the second claim, we start with the expression $\langle (\hat{Q} - \langle \hat{Q} \rangle)^2 \rangle$ and plug in the definition of an expectation value: we find that

$$(\Delta\hat{Q})^2 = \int \Psi^*(x)(\hat{Q} - \langle \hat{Q} \rangle)^2\Psi(x)dx = \int \Psi^*(x)(\hat{Q} - \langle \hat{Q} \rangle)(\hat{Q} - \langle \hat{Q} \rangle)\Psi(x)dx.$$

We now think of the first $(\hat{Q} - \langle Q \rangle)$ as an operator acting on the rest of the integrand – because \hat{Q} is Hermitian and so is $\langle Q \rangle$ (multiplying by a **real** constant is equivalent no matter which part of the integrand it's done on), the whole

term $(\hat{Q} - \langle Q \rangle)$ is Hermitian, and thus by the definition of Hermiticity we have

$$= \int ((\hat{Q} - \langle Q \rangle)\Psi(x))^* (\hat{Q} - \langle Q \rangle)\Psi(x) dx = \int |(\hat{Q} - \langle Q \rangle)\Psi(x)|^2 dx,$$

as desired. □

Notice that our second claim in fact writes the uncertainty $(\Delta\hat{Q})^2$ as an integral of a positive quantity, meaning that $\Delta\hat{Q}$ is always real.

Corollary 81

A state Ψ is an eigenstate of a Hermitian operator \hat{Q} (meaning that $\hat{Q}\Psi = \lambda\Psi$) if and only if $(\Delta\hat{Q})^2 = 0$. In addition, we have $\lambda = \langle \hat{Q} \rangle$ (so that we can write $\hat{Q}\Psi = \langle \hat{Q} \rangle \Psi$).

Proof. We show the second claim first: to do so, we integrate

$$\langle \hat{Q} \rangle = \int \Psi^* \hat{Q} \Psi dx = \int \Psi^* \lambda \Psi dx = \lambda \int |\Psi|^2 dx = \lambda,$$

so the eigenvalue is indeed the expectation of \hat{Q} . So now for the first claim, Ψ is an eigenstate of \hat{Q} if and only if $(\hat{Q} - \langle Q \rangle)\Psi = 0$, if and only if (by part two of Lemma 80, since the integral is only zero if the nonnegative integrand is always zero) $(\Delta\hat{Q})^2 = 0$, if and only if $\Delta\hat{Q} = 0$, as desired. □

We now have several different expressions for the uncertainty of an operator \hat{Q} , and they are each useful in different situations. For example, if we have a Gaussian wavefunction that is centered at the origin, then $\langle \hat{x} \rangle = 0$, so the easiest way to calculate the uncertainty in position is

$$(\Delta x)^2 = \langle x^2 \rangle - \langle x \rangle^2 = \langle x^2 \rangle,$$

and that's just a Gaussian integral for us to do. And now that we've defined uncertainty, we can actually state the uncertainty principle precisely: we're saying that $\Delta x \Delta p \geq \frac{\hbar}{2}$ under the mathematically rigorous definition.

We'll now move on to our next topic, **stationary states**, which will keep us busy for a few weeks as we develop intuition for solving the Schrodinger equation.

Definition 82

A **stationary state** is a solution to Schrodinger's equation with factorized space and time dependence

$$\Psi(x, t) = g(t)\psi(x).$$

Note that these solutions **aren't static** – they do have time-dependence, but that time-dependence is very simple. From here on, we'll be careful to use the capital letter Ψ for full wavefunctions with time-dependence and lowercase ψ for the time-independent wavefunctions.

The reason these states are called "stationary states" is that **time-independent observables will not have time-dependence in expectation value** if we have a state Ψ of this form. We'll see this in a few minutes, but first let's use a "separation of variables" technique for solving differential equations to understand $\Psi(x, t)$ more generally. Plugging in this stationary state into Schrodinger's equation, we start with

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = \hat{H}\Psi(x, t) = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \Psi(x, t).$$

Fact 83

We're considering here systems where the potential $V(x)$ does **not** depend on time – otherwise, if the “landscape” of our problem is changing, we can't easily get stationary states.

Substituting $\Psi(x, t) = g(t)\psi(x)$, we find that because the left-hand side only acts on the time-coordinate and the Hamiltonian on the right-hand side only acts on the space-coordinate,

$$i\hbar\psi(x)\frac{dg(t)}{dt} = g(t)\hat{H}\psi(x),$$

where $\hat{H}\psi(x)$ is again just a function of x . Rearranging by dividing the whole equation by Ψ , we find that

$$i\hbar\frac{1}{g(t)}\frac{dg(t)}{dt} = \frac{1}{\psi(x)}\hat{H}\psi(x).$$

Since the left-hand side is now only a function of time, and the right-hand side is only a function of space, the only way for these to be equal in general is that **both sides are constant**, and we'll call that constant E . This E must have units of energy (because those are the units of \hat{H} and also of $\frac{\hbar}{\tau}$), and it must be real – we'll see later that if we try to choose E to be complex, we'll run into problems.

But for now we'll go ahead and solve the two (decoupled) differential equations: we have

$$i\hbar\frac{dg(t)}{dt} = Eg(t) \implies g(t) = Ce^{-iEt/\hbar},$$

and thus the time-dependence of a stationary state is just the phase $e^{-iEt/\hbar}$. On the other hand, the other equation becomes

$$\hat{H}\psi(x) = E\psi(x) \implies \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \right) \psi(x) = E\psi(x)$$

(we can use a normal derivative now that we have just functions of a single variable). So the rest of the problem is still complicated – we still need to solve the second-order differential equation for $\psi(x)$, and this is called the **time-independent Schrodinger equation**. What's interesting is that when we solve this differential equation, we often find that we are constrained to **particular** values of E (if we think about the analogy with matrices, the equation $\hat{H}\psi(x) = E\psi(x)$ is really an eigenfunction equation, and matrices often only have a discrete set of eigenvalues).

Putting things together, we find that once we solve the time-independent Schrodinger equation, we arrive at the full wavefunction

$$\Psi(x, t) = C\psi(x)e^{-iEt/\hbar}.$$

If we try to normalize this state, we can just normalize using ψ (meaning that we **absorb C into the time-independent solution**). Thus, we are asking for

$$1 = \int \Psi^*(x, t)\Psi(x, t)dx = \int \psi^*(x)e^{iEt/\hbar}\psi(x)e^{-iEt/\hbar}dx.$$

But the phase terms $e^{iEt/\hbar}$ and $e^{-iEt/\hbar}$ cancel out here, so in fact the condition for normalization is just

$$\int \psi^*(x)\psi(x)dx = 1,$$

and we can just check normalization for ψ . In particular, the time-dependence doesn't end up making a contribution for normalization, and **this is the key reason why we want E to be real** – if the energy weren't real, the complex conjugate of $e^{iEt/\hbar}$ would not just be $e^{-iEt/\hbar}$, so we'd have a function of t that would also need to be equal to 1 on

the left-hand side. Thus, stationary states must have real E if we want to consider them in actual physical contexts (where we do need normalized states to say meaningful things).

We'll now check out properties of the Hamiltonian operator \hat{H} , and we'll indeed see that this is all connected to energies and energy eigenstates. If $\Psi(x, t)$ is a stationary state, then

$$\langle \hat{H} \rangle_{\Psi(x,t)} = \int \Psi^*(x, t) \hat{H} \Psi(x, t) dx = \int \psi^*(x) e^{iEt/\hbar} \hat{H} e^{-iEt/\hbar} \psi(x),$$

and again the time-dependence cancels out because $e^{-iEt/\hbar}$ is a constant from the point of view of \hat{H} . Thus, this expectation is just

$$= \int \psi^*(x) \hat{H} \psi(x) = \langle \hat{H} \rangle_{\psi(x)};$$

that is, **the expectation value of the Hamiltonian on the full stationary state is the expectation value of the Hamiltonian on just the spatial part**. And furthermore, because we have the eigenvalue equation $\hat{H}\psi(x) = E\psi(x)$, we can further evaluate this to be

$$= \int \psi^*(x) E \psi(x) = \boxed{E}.$$

So the expectation value of the Hamiltonian is in fact equal to the energy E , and the $\psi(x)$ s are the energy eigenstates of \hat{H} . (And there is no uncertainty in the measured energy either, because $\langle \hat{H}^2 \rangle = \langle \hat{H} \rangle^2 = E^2$.)

More generally, we can now verify the claim from above:

Proposition 84

The expectation value of any time-independent operator \hat{Q} in a stationary state $\Psi(x, t)$ is time-independent.

Proof. In exactly the same way,

$$\langle \hat{Q} \rangle_{\Psi(x,t)} = \int \Psi^*(x, t) \hat{Q} \Psi(x, t) dx = \int \psi^*(x) e^{iEt/\hbar} \hat{Q} \psi(x) e^{-iEt/\hbar} dx,$$

and now because of commutativity, we can move the $e^{-iEt/\hbar}$ term past the $\psi(x)$ and \hat{Q} terms to cancel with the $e^{iEt/\hbar}$ and remove the time-dependence:

$$= \int \psi^*(x) \hat{Q} \psi(x) dx = \langle \hat{Q} \rangle_{\psi(x)},$$

which is time-independent because no t shows up in the final expression. □

Fact 85

Note that in general, the superposition of two stationary states is **not** a stationary state, because we can't factor $\Psi_1(x, t) + \Psi_2(x, t)$ if the time-components $e^{iEt/\hbar}$ look different (that is, if the energies E are different).

In particular, if we take an expectation of a time-independent operator in a **superposition** of stationary states, we now no longer necessarily have time-independence of that expectation value. Quantum mechanics would be very boring if all expectation values were always constant, and indeed this superposition is how time-dependence ends up occurring in general.

We'll now turn to solving the time-independent equation $\hat{H}\psi(x) = E\psi(x)$ for some arbitrary potential $V(x)$. Because this is an eigenvalue equation for a Hermitian operator \hat{H} , we have the results from our last lecture: the eigenfunctions can be chosen to form an orthonormal set of functions that span the whole space of (spatial) wavefunctions. With that, we are able to obtain the **spectrum** of the theory (which is the set of eigenvalues and eigenstates

associated to the particular Hamiltonian \hat{H}). And remember that finding the energy eigenstates ψ_1, ψ_2, \dots and the associated energy eigenvalues is basically the gold standard for what we want to do, because from there we can write any arbitrary state as a superposition of the ψ_i s. The spectrum may be discrete, or there may be a set of continuous allowed energies, but for any problem (for instance, any potential $V(x)$ that we might be given), our goal is always to find out what that spectrum is.

We'll slightly rewrite the second-order differential equation that we're trying to solve: we are looking for functions $\psi(x)$ that satisfy

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}(V(x) - E)\psi(x).$$

The potential $V(x)$ can take on many forms – it might be smooth, or it might have discontinuities and kinks, or it may have delta functions or infinite jumps. We'll accept all of these different cases in our considerations, because potentials can be as strange as we can imagine depending on the problem that we're trying to solve. (But there are worse cases, such as potentials discontinuous at every point or derivatives of delta functions, and we won't think about those cases.) The key is that for each of the different possible kinds of behavior for $V(x)$, we want to understand the **boundary conditions that are being imposed** on our solution $\psi(x)$. What we really care about is properties of ψ' and ψ , because those are what allow us to stitch together solutions at interfaces and discontinuities of V .

Proposition 86

For a potential $V(x)$ as described above, we have the following:

- The wavefunction $\psi(x)$ must be continuous at all x .
- $\psi'(x)$ is continuous unless $V(x)$ contains a delta function.

Proof. For the first point, if $\psi(x)$ had a discontinuity at some point, then $\psi'(x)$ would contain a delta function, and thus $\psi''(x)$ would contain the derivative of the delta function. But the right-hand side (involving $V(x)$) can only have a delta function at worst, so this is not allowed.

For the second point, we're equivalently saying that ψ' is discontinuous only if $V(x)$ has a delta function. Notice that $\psi'(x)$ is discontinuous only if $\psi''(x)$ has a delta-function in it; since ψ itself is continuous (by our above argument), the only way for $\frac{2m}{\hbar^2}(V(x) - E)\psi(x)$ to have a delta-function in it is if $V(x)$ does. \square

With this, we're finally ready to move on to solve the Schrodinger equation in some particular cases. Our first example is one that we've already briefly touched on:

Example 87 (Particle on a circle)

Consider a particle on a circle of total circumference L – equivalently, we can think of solving the Schrodinger equation on the real line with the additional condition that points x and $x + L$ are identified with each other. To make life simple, we'll have **zero potential** $V(x) = 0$.

In other words, $x = 0, L, 2L, 3L, \dots$ all correspond to the same point on the circle, and it's equivalent to think of a circle as "infinitely many copies" of whatever happens between 0 and L also occurring between L and $2L$, $2L$ and $3L$, and so on. Thus, we have the boundary condition

$$\psi(x + L) = \psi(x).$$

Because we have zero potential, our Hamiltonian is $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$, and the time-independent Schrodinger equation we

must solve is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \iff \boxed{\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi}.$$

We claim that all solutions to this equation must have $E \geq 0$. To see this, notice that if we “multiply both sides by $\int_0^L \psi^* dx$,” we have

$$-\frac{\hbar^2}{2m} \int_0^L \psi^*(x) \frac{d}{dx} \frac{d}{dx} \psi(x) dx = E \int_0^L \psi^*(x) \psi(x) dx.$$

Assuming that ψ is a well-normalized solution, the right-hand side simplifies to E , and now typically we will apply integration by parts to the left-hand side. But we’ll do it slowly here: we can verify by the product rule that we can rewrite as

$$-\frac{\hbar^2}{2m} \int_0^L \left[\frac{d}{dx} \left(\psi^* \frac{d\psi}{dx} \right) - \frac{d\psi^*}{dx} \frac{d\psi}{dx} \right] dx = E.$$

The first term in the bracket is now a total derivative, so integrating that term from 0 to L (and using that $\frac{d\psi^*}{dx}$ is the conjugate of $\frac{d\psi}{dx}$) gives us

$$-\frac{\hbar^2}{2m} \psi^* \frac{d\psi}{dx} \Big|_0^L + \frac{\hbar^2}{2m} \int_0^L \left| \frac{d\psi}{dx} \right|^2 dx = E.$$

But because we’re on a circle here, the points L and 0 are the same point, and thus the boundary term vanishes! (Importantly, we cannot make arguments about ψ going to 0 at the boundary here – we are using the geometry of the problem.) Thus, we find that E is the integral of some positive quantity, and thus the energy is always nonnegative, as claimed.

We’ll finish solving this differential equation next time, but for now we’ll just write down a few solutions: looking back at the boxed equation above, we’ll make the definition

$$-\frac{2mE}{\hbar^2} = -k^2, \quad k \in \mathbb{R}.$$

We know that the left-hand is indeed negative, so this is a valid definition of the constant k , and furthermore we can rearrange to find that $E = \frac{\hbar^2 k^2}{2m}$, which is $\frac{p^2}{2m}$ if $p = \hbar k$. So our notation is actually very good here – the constant k that we’ve defined is actually such that $\hbar k$ is the momentum of the particle! So all that’s left to solve is

$$\frac{d^2\psi}{dx^2} = -k^2\psi,$$

and this is the usual **wave equation**, solved by sines and cosines or by exponentials. For convenience, we’ll use solutions of the form $\psi = e^{ikx}$, and next time we’ll see which values of k work and how to normalize these wavefunctions!

Lecture 11: The Infinite and Finite Square Well

Today’s lecture is dedicated to solving the Schrodinger equation for certain potentials $V(x)$, beginning to give us insight into the kinds of solutions that we will see in various physical settings. We’ll start by finishing the particle on a circle problem, and then we’ll discuss the infinite and finite square wells.

Recall from last time that a particle on a circle can be represented by a particle on the real line, where we identify x with $x + L$ for any real number x . Thus, we want wavefunctions that are periodic mod L (that is, $\psi(x + L) = \psi(x)$ and thus the same is true for the derivative ψ'), and last time we found that for zero potential $V(x) = 0$, solutions are of the form $\psi(x) \sim e^{ikx}$, where $k^2 = \frac{2mE}{\hbar^2}$ for some $E \geq 0$.

Our next step is to apply the periodicity condition: since $\psi(x + L) = \psi(x)$, we must have

$$e^{ik(x+L)} = e^{ikx} \implies e^{ikL} = 1 \implies kL = 2\pi n$$

for some integer n . We'll index the allowed values of k as $k_n = \frac{2\pi n}{L}$, and from this we find that the n th momenta and energy levels are

$$p_n = \hbar k_n = \frac{2\pi\hbar n}{L}, \quad E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2}{2m} \cdot \frac{4\pi^2 n^2}{L^2} = \frac{2\pi^2 \hbar^2 n^2}{mL^2}.$$

To find our energy eigenstates, we now just need to find the normalization constants for $\psi_n(x) \sim e^{ik_n x}$. And here's where it's nice that our particle is on a circle rather than on a line: exponentials like this have $|e^{ik_n x}|^2 = 1$, so we would not be able to normalize the integral over all real numbers, but we can normalize the integral over the range $[0, L]$. Explicitly, the way we do this is to write $\psi_n(x) = Ne^{ik_n x}$, and then require

$$1 = \int_0^L |\psi_n(x)|^2 dx = \int_0^L N^2 dx = LN^2 \implies N = \frac{1}{\sqrt{L}}.$$

(Note that we can choose N to be positive real – an overall phase doesn't change the state.) This gives us our final answer:

$$\psi_n(x) = \frac{1}{\sqrt{L}} e^{ik_n x} = \frac{1}{\sqrt{L}} e^{2\pi i n x / L}.$$

Thus, we've found the energy eigenstates for the time-independent Schrodinger equation, and to obtain our stationary states, we must add in the time phase: for each n , we have

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

One important point to address here is that as we've stated so far, n can be any integer (positive, negative, or zero). Indeed, the momentum of these states, $\frac{2\pi\hbar n}{L}$, are different for all values of n , so they must be different states (and we don't have any additional degeneracy where different values of n are actually the same state). We might also be suspicious about $n = 0$, but that just corresponds to the wavefunction $\psi_0 = \frac{1}{\sqrt{L}}$, which has no x -dependence and thus no energy or momentum – this is all consistent with the Schrodinger equation we are trying to solve.

However, notice that states ψ_n and ψ_{-n} have the same energy $E_n = E_{-n}$, so they are in fact **degenerate energy eigenstates**. The important concept to keep in mind is the following:

Fact 88

If we have two energy eigenstates of the same energy, there must be something physical that distinguishes them, and we must figure out what that is to get a full picture of the physics of our system.

In our case, we've already figured that out – states ψ_n and ψ_{-n} have different momenta p_n and $-p_n$ (informally one represents the "particle moving to the right" and the other represents the "particle moving to the left"). And this additional physical quantity is also good for us because it tells us that ψ_n and ψ_{-n} are orthonormal – even though they are degenerate in energy, they are eigenstates of the Hermitian operator \hat{p} of different momenta, so their inner product is indeed zero.

Remark 89. *If we hadn't known about the momentum, we would potentially have had to do some additional work with each ψ_{-n} and ψ_n , finding linear combinations until we get two orthonormal states of energy E_n . And if we had tried to use sines and cosines instead of exponentials when we solved this problem, that's what we would have encountered.*

Putting everything together, we've thus found an orthonormal set of states which spans our time-independent

wavefunctions. So if we're given any periodic $\psi(x)$ (any wavefunction on the circle), we can write

$$\psi(x) = \sum_{n \in \mathbb{Z}} a_n \psi_n(x).$$

Furthermore, notice that $\psi_k + \psi_{-k} \sim \cos(kx)$ and $\psi_k - \psi_{-k} \sim \sin(kx)$, so we can always rewrite our wavefunction $\psi(x)$ as a sum of sines and cosines as well. Either way, this is secretly getting back to Fourier's theorem and Fourier series: any periodic function can be written as a sum of sines and cosines, or as a sum of appropriate exponentials.

We're now ready to move on to our next problem of the day:

Example 90 (Particle in a box)

Suppose we have a particle in one dimension constrained to the segment $x \in [0, a]$, where there are **hard walls** to the left and right of this segment that the particle cannot cross. In other words, we have

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

To solve this problem, first notice that if the potential is infinite outside the interval $[0, a]$, then the wavefunction must be zero there as well. Informally, this is because being in an area of infinite potential requires infinite energy – if we want to be more rigorous with that, we can solve the problem with a finite potential outside $[0, a]$ and take that potential to ∞ , and we will indeed see the finite square well solution later in this lecture. But for now, let's just assume

$$\psi(x) = 0 \text{ for } x < 0 \text{ and } x > a.$$

Furthermore, we can see that it does not really matter whether the potential V is zero or infinite at the endpoints – since we require that ψ is continuous by Proposition 86 we must also have $\psi(0) = \psi(a) = 0$ by continuity. So it suffices now to solve the free Schrodinger equation in the region $[0, a]$, and this is very similar to what we had before for the particle on a circle: we have

$$\psi''(x) = -\frac{2mE}{\hbar^2} \psi(x) = -k^2 \psi(x),$$

and this time it's more convenient to use sines and cosines instead of exponentials:

$$\psi(x) = c_1 \cos(kx) + c_2 \sin(kx).$$

This is because we can now impose boundary conditions – since $0 = \psi(0) = c_1$, the first term goes away, and then since $0 = \psi(a) = c_2 \sin(ka)$ and we can't also have $c_2 = 0$ (that would be a zero wavefunction), we must similarly have

$$ka = n\pi \implies k_n = \frac{\pi n}{a},$$

but this time we won't use all integers n – first of all, $n = 0$ makes the wavefunction vanish, which is not allowed. (It was allowed for the exponential because $n = 0$ gave us a nonzero constant there, but having the wavefunction be identically zero means we have no probability of finding the particle anywhere.) In addition, taking k_n or k_{-n} gives us **the same wavefunction up to a sign**, because $\sin(k_n x) = -\sin(-k_n x)$. Thus, we instead index our particle-in-a-box states by integers $\boxed{n \geq 1}$, and all that's left is to normalize. Writing $\psi_n(x) = N \sin\left(\frac{n\pi x}{a}\right)$, we have

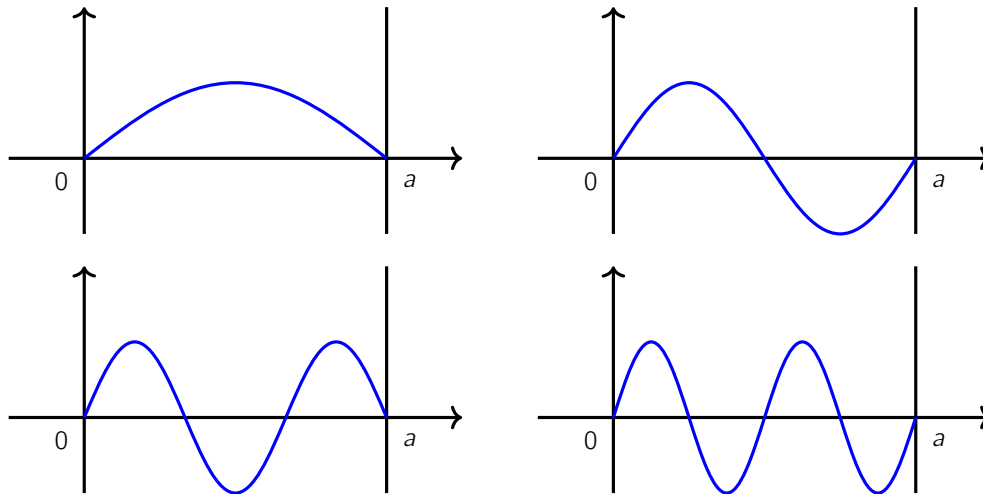
$$1 = \int |\psi_n(x)|^2 dx = N^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx,$$

and we can either do the integral using double-angle identities or note that the average value of \sin^2 over any half-period is $\frac{1}{2}$, so that $1 = N^2 \cdot \frac{a}{2} \implies N = \sqrt{\frac{2}{a}}$. This gives us our final equation for the energy eigenstates:

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right), \quad E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2ma^2}.$$

This time, every energy state (for $n \geq 1$) has different energy, so there are no degeneracies – in fact, the energy levels become more spaced out as n gets larger.

We'll now extract a few more properties of these infinite square well eigenstates, particularly looking at **nodes and symmetries**. Here are some sketches of the first 4 (smallest) energy eigenstates:



Notice that each time we add 1 to n , moving up to the next energy eigenstate, the argument of the sin at $x = a$ increases by π , meaning that we gain another half-wavelength per energy level. We call ψ_1 the **ground state**, because it has the lowest energy out of any eigenstate, and we can notice that the ground state has **no nodes** (that is, no points in the interior, not including the endpoints or infinity, where the wavefunction is zero). Then the next excited state has one node, the one after that has two nodes, and so on. This behavior with nodes is actually a general result for potentials with bound states (that is, normalizable states that decay to zero) – the number of nodes will increase with the energy of the eigenstate. We won't do a very rigorous proof of this result in this class, but we will see some strong evidence of it through many of our examples.

Additionally, we can also pay attention to the symmetry of our energy eigenstates. For simplicity in setting up notation, we set up our infinite well between $x = 0$ and $x = a$, but it would have been potentially more enlightening to set it up between $x = -\frac{a}{2}$ and $x = \frac{a}{2}$ – in that case, we would have a potential $V(x)$ which is symmetric around $x = 0$. Correspondingly translating the four energy eigenstates above, notice that the first and third energy eigenstates are symmetric around $x = 0$, while the second and fourth are antisymmetric! This is also a general fact – if we have bound states in a symmetric potential V (satisfying $V(-x) = V(x)$), then all energy eigenstates are either odd or even. (We'll prove this in our next lecture.)

Finally, there's one more important property about bound states in a one-dimensional potential: **there are no degeneracies** for bound states as long as our potential spans the whole real line or has hard walls. (On the other hand, this assumption did not hold for the particle on a circle because of the identification we performed, so that's why degeneracy is possible in that case.) Basically, the point of covering the infinite square well is for us to start seeing these kinds of general behaviors for wavefunctions satisfying the Schrodinger equation, and we'll go into more detail about them in the coming lectures.

With that, we'll turn to our final example of the lecture, where for the first time we won't be able to write down the solutions directly and will sometimes need to use numerical methods. This time, we'll set it up so that we have a symmetric potential:

Example 91 (Finite square well)

Suppose we have a particle in one dimension with a dip between $x = -a$ and $x = a$: more specifically, our particle is placed in the potential

$$V(x) = \begin{cases} 0 & x \leq -a, \\ -V_0 & -a < x < a, \\ 0 & x \geq a. \end{cases}$$

for some constant $V_0 > 0$.

We will look for **bound states**, which are normalizable solutions that tend to remain in a particular region (definition to come next lecture). In particular, thinking of this potential classically, if our state is at energy $E < 0$ and is localized at the origin (inside the well), then it requires some additional energy to escape the well and get to an energy of 0. So what we'll end up finding with the wavefunction is that a bound state (with energy between 0 and $-V_0$) will have some small but nonzero probability of being found outside the well.

Remark 92. *It turns out that there are never any solutions to the Schrodinger equation if the energy E of our state is lower than any point in the potential (so in this case, there are no states of energy $E < -V_0$).*

Recall that our Schrodinger equation can be written as

$$\psi'' = -\frac{2m}{\hbar^2}(E - V(x))\psi,$$

and this is the first time where we have a nonzero $V(x)$ that we must consider when solving the equation. The total energy of a particle can be thought of as the potential plus kinetic energy, so the amount that E exceeds $-V_0$ gives us the kinetic energy of the particle inside the square well. But with that analogy, we have "negative kinetic energy" for the particle outside the well, which is impossible classically. As we do this calculation, we'll see how this all works out with the "leaking probability" outside the well, and we'll see that if the barrier gets arbitrarily high, then the wavefunction will get closer and closer to the one for the infinite square well.

We'll now set up the problem and work towards finding the energy eigenstates. The difference between our energy E and the well potential energy $-V_0$ is

$$E - (-V_0) = V_0 + E = V_0 - |E|$$

(remember that we're taking $E < 0$), and because our potential $V(x)$ is **piecewise constant**, we can solve the Schrodinger equation in each region and patch the solutions together – in each case, we have an equation of the form $\psi'' = \alpha\psi$ for some constant α . Inside the well, we have $\alpha < 0$, meaning that solutions will be trigonometric functions, while outside the well, we have $\alpha > 0$, meaning that solutions will be real exponentials. And when we try to stitch those different forms together into a continuous wavefunction, we expect that we'll get some **quantization of allowed energies**, because that was indeed the case in the infinite square well as well.

We'll use the result that symmetric potentials will always give us even or odd solutions for $\psi(x)$, and we'll first look for **even solutions** (where $\psi(x) = \psi(-x)$). The key to having a nice solution here is to make good use of **unit-free numbers** – we'll make lots of definitions and it won't look like we're solving anything for a while, and then

suddenly we'll see the solution pop up. For an even solution in the region $-a < x < a$, we're asking for a solution to

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}(E - (-V_0))\psi = -\frac{2m}{\hbar^2}(V_0 - |E|)\psi.$$

We'll define $k^2 = \frac{2m}{\hbar^2}(V_0 - |E|) > 0$, so that our differential equation becomes

$$\psi'' = -k^2\psi \implies \boxed{\psi(x) = \cos(kx) \text{ for } -a < x < a},$$

the key here being that we only have cosine (and not sine) because we assume our solutions are symmetric. We won't normalize our solutions because they're pretty messy (it's not necessary for obtaining energy eigenstates anyway). Instead, we'll normalize by fixing the constant of $\cos(kx)$ to be 1 – this gives us the form of the wavefunction inside the well, and now we turn to the wavefunction outside the well. Then because $V(x) = 0$ in this region, we have

$$\psi'' = -\frac{2mE}{\hbar^2}\psi = \frac{2m|E|}{\hbar^2}\psi = \kappa^2\psi,$$

where we define the positive constant $\kappa^2 = \frac{2m|E|}{\hbar^2}$. Our solutions are then exponentials: $\psi(x) \sim e^{\pm\kappa x}$, and thus we must have

$$\boxed{\psi(x) = Ae^{-\kappa x} \text{ for } x > a, \quad \psi(x) = Ae^{\kappa x} \text{ for } x < -a}$$

for some positive constant A . Furthermore, notice that we have the constraining relation

$$\kappa^2 + k^2 = \frac{2mV_0}{\hbar^2},$$

and now we can rewrite it to be unitless: multiplying through by a^2 gives us

$$k^2 a^2 + \kappa^2 a^2 = \frac{2mV_0 a^2}{\hbar^2}.$$

(We shouldn't lose track of our goal – we want to find the allowed energies E .) We'll now define the unit-free constants

$$\boxed{\xi = \kappa a > 0, \quad \eta = ka > 0, \quad z_0^2 = \frac{2mV_0 a^2}{\hbar^2}},$$

so that we have $\boxed{\eta^2 + \xi^2 = z_0^2}$. It might look like all we've done is traded k, κ for unitless constants η, ξ , but it turns out that z_0 is an important quantity which encodes the physical parameters of our system (it's large if the well is deep or wide and small if the well is shallow or narrow) and actually **is all we need to calculate the number of bound states in our well**. We'll soon see that z_0 being large gives us many bound states, while z_0 being small gives us very few of them!

Turning back to calculations, we know that our wavefunction ψ and its derivative ψ' must be continuous at $x = a$ (and also $x = -a$, but it's sufficient to check the former because we know our solution is even). We thus require that

$$\cos(ka) = Ae^{-\kappa a}, \quad -k \sin(ka) = -\kappa Ae^{-\kappa a}.$$

Dividing the second equation by the first and then multiplying by a on both sides gives us

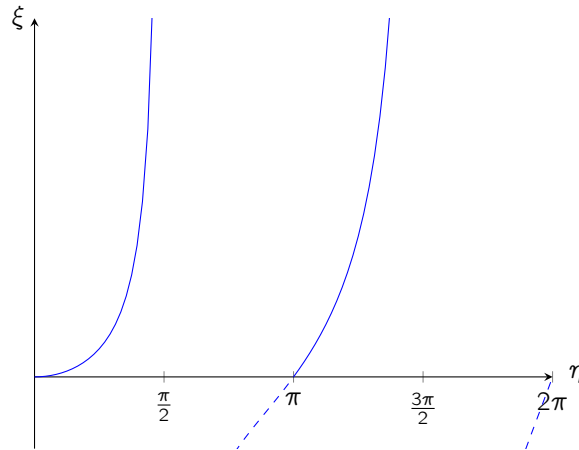
$$k \tan ka = \kappa \implies ka \tan ka = \kappa a \implies \boxed{\eta \tan \eta = \xi}.$$

Thus, our problem has now reduced to finding either η or ξ , from which all of the other constants in the problem will

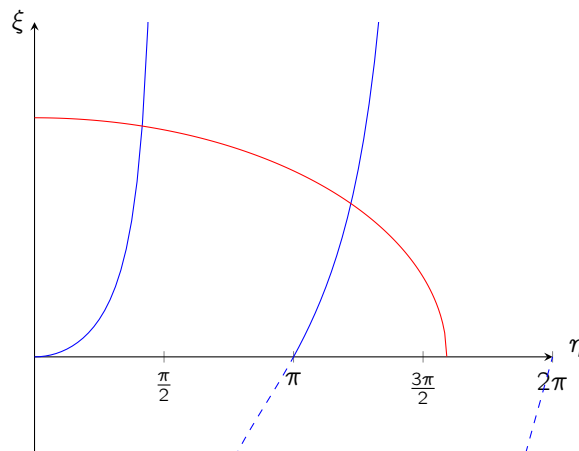
follow (since we know z_0^2 and a from the physical parameters). Notice that

$$\xi^2 = \kappa^2 a^2 = \frac{2m|E|a^2}{\hbar^2} = \frac{2mV_0 a^2}{\hbar^2} \frac{|E|}{V_0} = z_0^2 \frac{|E|}{V_0} \implies \boxed{\frac{|E|}{V_0} = \left(\frac{\xi}{z_0}\right)^2};$$

in other words, we can get a dimensionless measure of the energy (which essentially tells us the proportionality constant between the depth of the well and our energy) in terms of our newly defined constants! And now we're ready for the final answer: if we graph η, ξ in their first quadrant (since we know they must both be positive), then the condition $\xi = \eta \tan \eta$ looks as shown below:

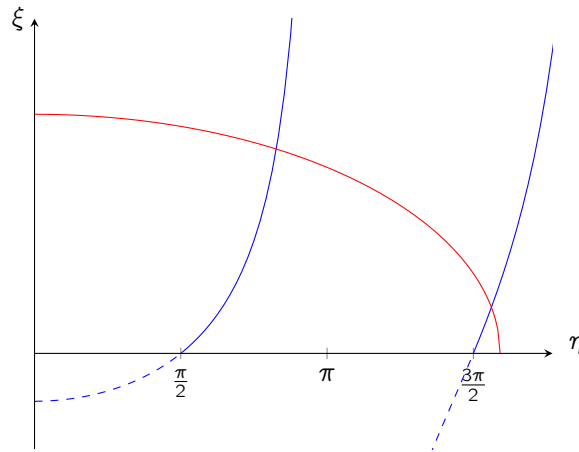


Then the other curve $\xi^2 + \eta^2 = z_0^2$ is just the circle of radius z_0 centered at the origin, and we want to find the points where these two curves intersect. For example, here's the situation for $z_0 = 5$ (it looks like an ellipse below because the axes are scaled differently):



And just looking at this graph, we can count the number of bound states by looking at how many points to intersection we have, which is given by **the number of multiples of π smaller than z_0** (because each of those blue branches gives us one intersection). In particular, notice that there will always be a bound state for any positive value of z_0 ! Furthermore, because z_0 is fixed and we have the boxed relation between ξ and z_0 above, the leftmost solution corresponds to the **most deeply bound state** (and thus the state of lowest energy), and going from left to right gives us the states in increasing order of energy.

We've thus solved the finite square well for the **even solutions** case – a similar solution method works for the odd solutions case, but in that case we have $\xi = -\eta \cot \eta$:



Thus, the odd solutions don't always exist – the potential V_0 must be sufficiently deep for us to have them, and with a bit more inspection we can see that the even and odd solutions will interleave for the finite square well. The main lesson that we should learn here is the power of unit-free constants and how they can tell us when solutions exist!

Lecture 12: Qualitative Properties of Eigenstates, Local Picture of the Wavefunction, and the Shooting Method

Last lecture, we computed the energy eigenstates for a few special potentials $V(x)$. In general, if we're faced with an arbitrary potential, we likely want to know the key features of the resulting eigenstates, and we'll explore those kinds of qualitative considerations today.

We'll start with three key properties of wavefunctions that are inspired by some of the examples from last lecture:

Definition 93

A **bound state** is a normalizable energy eigenstate over the real line (meaning that $\psi \rightarrow 0$ as $x \rightarrow \pm\infty$).

The idea is that if a wavefunction goes to 0 at infinity, then it has a bump in the middle at some point, so the potential is "keeping the particle bound."

Proposition 94

For one-dimensional potentials over the real line, there are no nondegenerate bound states.

(This is left as an exercise for us – it's a problem in Griffiths.) The second result is related to the fact that we were able to construct our wavefunctions to be real-valued, even though generally the full wavefunction is complex-valued. Essentially, just like we saw in last lecture, often we can encode all of the complex-valued behavior in just the phase $e^{-iEt/\hbar}$, because the time-independent Schrodinger equation $\hat{H}\psi = E\psi$ has no i in it:

Proposition 95

Energy eigenstates of the time-independent Schrodinger equation, where $V(x)$ is real, can be chosen to be real.

What this result says is that in general, we can always **have the possibility** to work with real solutions for our energy eigenstates.

Proof. Consider the Schrodinger equation $\hat{H}\psi = E\psi$. If we take the complex conjugate of both sides, we obtain $\hat{H}\psi^* = E\psi^*$ (because the potential $V(x)$ is real, we can check that $(\hat{H}\psi)^* = \hat{H}\psi^*$). Thus, ψ^* and ψ are two energy eigenstates of the same energy. If they are linearly independent, then taking $\psi_r = \frac{1}{2}(\psi^* + \psi)$ and $\psi_i = \frac{1}{2i}(\psi - \psi^*)$ gives us two new real, linearly independent energy eigenstates of the same energy (which we can work with instead). And if ψ^* and ψ start off linearly dependent, then we just have one unique energy eigenstate, and at least one of those linear combinations is nonzero. Thus we can always form enough new energy eigenstates that are real as long as $V(x)$ is real. \square

Essentially, these linear combinations of ψ and ψ^* , which we denoted ψ_r and ψ_i , give us the real and imaginary parts of ψ , and both of those parts turn out to be solutions to the (time-independent) Schrodinger equation.

Corollary 96

All bound states in one-dimensional potentials are real up to a phase.

Proof. Proposition 95 tells us that all energy levels are nondegenerate. Following the proof of Proposition 95, ψ and ψ^* must then be proportional to avoid degeneracy. Thus the real and imaginary parts are also proportional to each other, so the full wavefunction ψ is just a complex number times its real part (which is a real wavefunction up to a phase). \square

This is a strong statement – we're essentially forced to work with real solutions for one-dimensional potentials, and the only complex part of the full wavefunction comes in the time-evolution term $e^{-iEt/\hbar}$ of our stationary states.

Our third result will be the one that we used last lecture to solve for energy eigenstates of the finite square well:

Proposition 97

If a one-dimensional potential $V(x)$ is even (that is, $V(x) = V(-x)$), then the energy eigenstates can be chosen to be either even or odd (under $x \mapsto -x$).

Proof. We wish to solve the equation

$$\psi''(x) + \frac{2m}{\hbar^2}(E - V(x))\psi(x) = 0.$$

(Here, note that $\psi''(x)$ denotes the second derivative of ψ , evaluated at x .) We essentially wish to show that $\psi(-x)$ solves the same equation, and we'll make sure we're clear with what's going on when we make that substitution. Let $\phi(x) = \psi(-x)$, so that the chain rule gives

$$\frac{d\phi(x)}{dx}(x) = \psi'(-x) \cdot -1 = -\psi'(-x), \quad \frac{d^2\phi}{dx^2}(x) = -\psi''(-x) \cdot -1 = \psi''(-x).$$

Thus, evaluating the original time-independent Schrodinger equation at $-x$ yields

$$\psi''(-x) + \frac{2m}{\hbar^2}(E - V(-x))\psi(-x) = 0,$$

and now replacing ψ s with ϕ s and noting that $V(-x) = V(x)$ yields

$$\phi''(x) + \frac{2m}{\hbar^2}(E - V(x))\phi(x) = 0,$$

which is the same Schrodinger equation but for ϕ . Thus, both $\psi(x)$ and $\phi(x) = \psi(-x)$ are solutions to the Schrodinger

equation **with the same energy**, so we can form the symmetric and antisymmetric parts of the wavefunction

$$\psi_s(x) = \frac{1}{2}(\psi(x) + \psi(-x)), \quad \psi_a(x) = \frac{1}{2}(\psi(x) - \psi(-x)),$$

which are even and odd, respectively, and by superposition they are also energy eigenstates of the same energy E . Thus we can use these symmetric and antisymmetric wavefunctions instead (and regardless of whether ψ and ϕ are linearly dependent or not, doing this operation preserves that fact). \square

Corollary 98

All bound states in one-dimensional potentials are either even or odd.

Proof. Again, Proposition 95 tells us that all energy eigenstates are nondegenerate, so the only choice we have for our eigenstates is multiplying by a constant (which does not change whether a function is even, odd, or neither). Thus the result above directly applies.

More specifically, $\psi(x)$ and $\psi(-x)$ must be proportional, and we can assume by Corollary 96 that $\psi(x)$ (and thus $\psi(-x)$) must be real. But if $\psi(-x) = c\psi(x)$, then $\psi(x) = c\psi(-x)$ by replacing x with $-x$ in the equation above. Thus $\psi(x) = c^2\psi(x)$, and thus $c = \pm 1$, corresponding to even and odd wavefunctions respectively. \square

This explains why our search for solutions of the finite square well last lecture was divided into two cases (symmetric and antisymmetric) – there are no other energy eigenstates that are possible. We'll be using this result in future lectures as well!

Now that we've established some general results, we'll turn to some qualitative insights of our (now established real) energy eigenstates. Whenever we have a problem with a potential V , we have a **total energy** $E = K + V$, and in our classical intuition energy is conserved, so both K and V are functions of x , but E is some fixed number. (And as V gets larger, K gets smaller, and vice versa.) Classically, if we know the kinetic energy of a particle, then we know its momentum (because $K = \frac{p^2}{2m}$). But we know that the corresponding de Broglie wavelength of the particle is $\lambda = \frac{h}{p}$, so given that the particle has some kinetic energy K , we should expect some kind of "wavelength" of λ to pop up in the wavefunction for our energy eigenstate. And all of that discussion is **exactly** true if our potential V is constant, because that's exactly how we derived the Schrodinger equation in the first place.

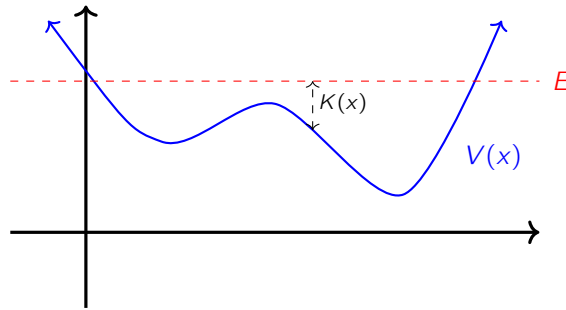
Example 99

Suppose we have a linearly growing potential $V(x)$ and some total energy E , so that as the particle moves to the right, its potential energy increases and thus its kinetic energy decreases.

Having the kinetic energy K decrease means that the momentum p gets smaller and that the "wavelength λ gets larger" (at least, we can say this if the potential is not growing too quickly, since that means V is approximately constant. Specifically, we can define a $K(x)$, $p(x)$, and $\lambda(x)$ in terms of the position of our particle x , and that means we predict that the wavefunction will oscillate more and more slowly as x increases. The exact formula for the solution to the Schrodinger equation in a linear potential relies on Airy functions and so on, so everything we're saying is **only approximate** but still useful (and if we plot the wavefunctions that's indeed what we'll see).

Example 100

Consider a potential $V(x)$ as in the diagram below – we'll try to extract some more qualitative features of the wavefunction, much like we've described above.



Classically, we know that the kinetic energy of a particle (represented by the black dashed line) cannot become negative, so the particle cannot move past either intersection point where $V(x) = E$. (Thus, there are regions on the left and on the right which is **classically forbidden**.) Those intersection points are called **turning points**, because in a classical setting those are the positions where (if we imagine a ball rolling around in the potential) the particle would stop and start turning back.

What we discussed above is basically that if our potential V were constant, then our wavefunction would take on a very simple form with a fixed wavelength λ . But if $V(x)$ varies slowly enough – that is, if the percentage change in $V(x)$ is small compared to the relevant distance $\lambda(x)$ – then we can speak of a “local wavelength.” This is actually getting to the discussion of the **WKB approximation**, which we discuss in 8.06, and the requirement is that

$$\lambda(x) \frac{dV}{dx} \ll V(x),$$

where $\lambda(x) = \frac{h}{p(x)} = \frac{h}{\sqrt{2mK(x)}}$ is the **local de Broglie wavelength** of the wavefunction at a position x . Really, all we’re saying is that if we were to sketch the wavefunction $\psi(x)$ corresponding to the potential $V(x)$ above, we’d generally have a faster oscillation where $V(x)$ is smaller and a slower oscillation where $V(x)$ is larger.

On the other hand, we can also discuss the amplitude of the wavefunction at these different positions, and this is connected to the **correspondence principle**. Basically, **if a particle spends more time in some region, then the wavefunction should have larger magnitude there**, so in the example above, we should spend more time where $V(x)$ is larger (because classically that corresponds to a smaller $K(x)$ and thus a smaller velocity for the particle). This turns out to be true, but we’ll explain it in a bit more detail.

The probability for a particle to be found in a region $[x, x + dx]$ is $|\psi(x)|^2 dx$, which is essentially proportional to the fraction of time $\frac{dt}{T}$ spent in this interval (where T is the total time in a period, if we imagine the particle rocking back and forth classically). Thus, we have

$$|\psi|^2 dx \sim \frac{dt}{T} = \frac{dx}{v(x)T} \implies |\psi|^2 \sim \frac{1}{p(x)} = \frac{\lambda(x)}{h},$$

so $|\psi| \sim \sqrt{\lambda(x)}$ – that is, in areas where the wavelength is longer and the potential $V(x)$ is larger, we will have a larger amplitude for the wavefunction $\psi(x)$. Combining this with our previous discussion, as well as the node theorem from last lecture (telling us how many times ψ intersects zero), we should now be able to estimate the wavelength and amplitude of a wavefunction, giving us a general sketch of ψ , without explicitly solving the Schrodinger equation.

We’re now ready to get the full local picture of the wavefunction: we can rewrite the time-independent Schrodinger equation as

$$\frac{1}{\psi} \frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2} (E - V(x)).$$

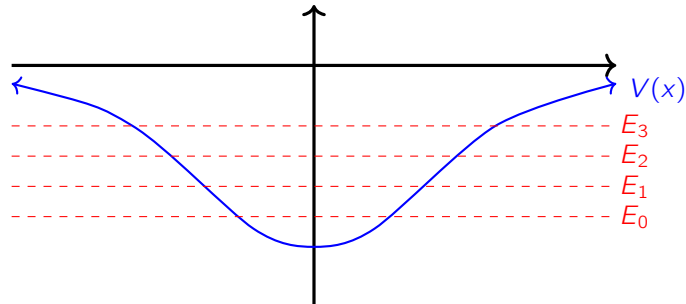
(Note here that ψ is an energy eigenstate of energy E .) We then have three cases to think about when trying to describe what ψ looks like (and remember that we can always treat it as real-valued):

- When $E - V(x) < 0$ (the **classically forbidden** region), the right-hand side is positive, so ψ and $\frac{d^2\psi}{dx^2}$ always have the same sign (unless ψ is zero). In other words, ψ is always **convex towards the axis** – if ψ is positive, then we have a “parabola going up,” and if ψ is negative, then we have a “parabola going down.” But since we’re in a classically forbidden region, the wavefunction should not get arbitrarily big – instead, what’s often actually happening is that our wavefunction is **asymptotically tending to zero** as $x \rightarrow \infty$ and $x \rightarrow -\infty$ (and thus the probability of finding the particle deeper into the classically forbidden region decays to zero as well).
- when $E - V(x) > 0$ (the **classically allowed** region), the right-hand side is negative, so ψ and $\frac{d^2\psi}{dx^2}$ have different signs. We can’t say anything asymptotically for this kind of behavior, but we should essentially imagine a sine function in the classically allowed region (downward parabola for ψ positive and upward parabola for ψ negative); basically, ψ is always **concave towards the axis**.
- When $E - V(x) = 0$ (one of the **turning points**), the right-hand side is zero, so either $\psi = 0$ or $\frac{d^2\psi}{dx^2} = 0$. This corresponds to having **inflection points** where ψ is nonzero (though notice that when ψ is zero, we also automatically have a point where the second derivative is zero). Thus, the key insight here is to remember that **inflection points of ψ occur at turning points and nodes**.

Example 101

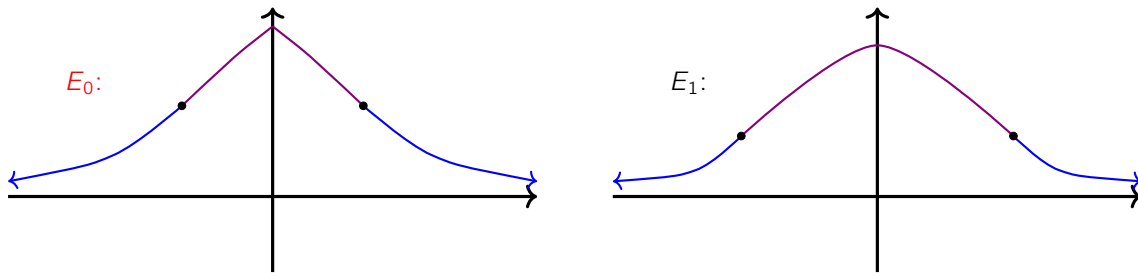
We’ll finish this lecture by returning to a generic smooth symmetric potential $V(x)$ and trying to understand its energy eigenstates.

Suppose that $V(x)$ looks as shown below, and as always we want to find bound states with some energy $E < 0$. We’ve labeled some example energies on the diagram below:

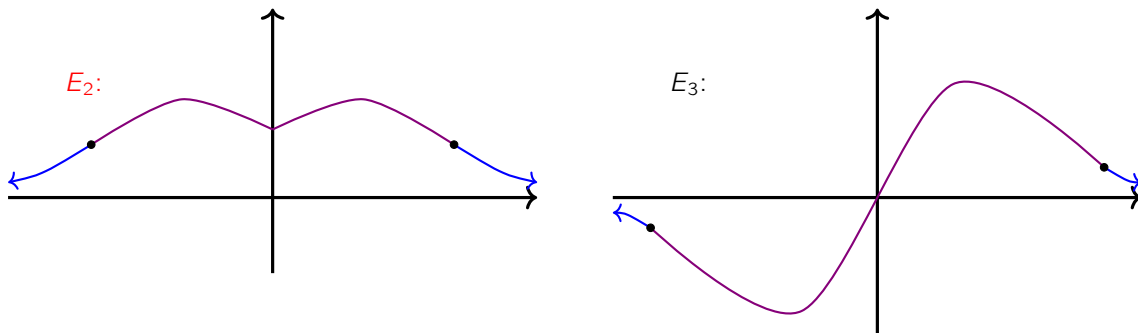


Because our wavefunction will always hit the classically forbidden region for large enough $|x|$, we know that ψ will decay asymptotically to zero on both the left and right side. Furthermore, we can choose ψ to be real-valued, and we can multiply it by a sign so that ψ is positive for large positive x (but decaying to 0), but depending on whether ψ is symmetric or antisymmetric, it may be negative or positive for large negative x .

We’ll try to get an understanding for **why a potential of this form naturally gives us energy quantization** by sketching the wavefunctions that would arise if we tried to form eigenstates at energy E_0, E_1, E_2 , and E_3 by numerically integrating from $-\infty$ and ∞ inward to 0. Each energy eigenstate will decay to zero at the endpoints, but between the turning points it will be concave towards the axis. For low energies, the turning points are close to the y-axis, and thus there isn’t enough time for ψ to turn all the way back to 0. This means we must have an even wavefunction, but the turning must happen in such a way that **the wavefunction does not have a discontinuity in the derivative** (because V is continuous). So it’s possible that in this example, the wavefunction formed by E_0 will not work as an energy eigenstate because of a kink, but the one formed by E_1 will, as shown below. (Turning points are labeled in black.)



In other words, as we slowly increase the energy E , we will finally get to a point where the curve flattens at $x = 0$, and that's our first energy eigenstate. If we continue to increase our energy, the turning points will move further out, and we will have even more time to curve back towards the x -axis. This means that we again will not have a valid wavefunction until the ψ we obtain hits the origin – **at that point**, we can obtain an antisymmetric solution as shown with the energy E_3 below.



So the second energy eigenstate occurs when the curve matches up to form an antisymmetric wavefunction. Further increasing the energy will create more oscillation in the purple (classically allowed) region, in such a way that for some higher energy E , ψ matches up with continuous derivative after two nodes. Repeating this process gives us higher and higher energy eigenstates – this is essentially the intuition for the node theorem and also for why energy is quantized!

Example 102

We can connect this argument to one other piece of intuition through the **shooting method** for solving differential equations.

If we have a symmetric potential and we're looking for even energy eigenstates, we can do the following procedure: pick some energy E_0 , and require $\psi(0) = 1, \psi'(0) = 0$. (We don't need to normalize our eigenstates, so we'll use this as the rescaling instead, and the reason for zero derivative is, just like above, to ensure that we have no kinks in ψ .) Since we have a second-order differential equation, these boundary conditions allow us to numerically integrate and find the wavefunction ψ for all x .

What we'll find typically is that after a while, ψ will start to blow up to $\pm\infty$ for large x , which is bad because that means we won't have a normalizable energy eigenstate. But if we change E slightly, we might find that ψ now blows up in the opposite direction $\mp\infty$ for large x . Then what that means is that in between our two values of E , there's a single point at which the wavefunction will decay, and that's the allowed energy eigenvalue for our potential $V(x)$!

Fact 103

Repeatedly searching in a smaller and smaller interval gives us the energy E to any arbitrary accuracy that we want, as long as Mathematica can still integrate for us, and the only thing we need to do is clean up our differential equation so that there are no units.

Lecture 13: The Delta Function Potential, Node Theorem, and Harmonic Oscillator

We'll start today by solving the Schrodinger equation for a new potential:

Example 104

Suppose we have a particle in one dimension placed in the potential $V(x) = -\alpha\delta(x)$ for some $\alpha > 0$ (this can be represented with a thick arrow pointing in the downward y -axis direction).

Essentially, we should imagine that we have a potential which is “infinitely negative” at $x = 0$, or equivalently the limit of a square well that gets deeper and narrower while keeping the area the same (which is in fact one way to analytically calculate the energy levels of this potential). Just like with the other potentials, we would like to calculate whether there are bound states (in this case, this means $E < 0$) and what their energy eigenvalues are for the corresponding Schrodinger equation.

It turns out we can discover a lot without having to do explicit calculations with the differential equation, and we do so by using our intuition and some of the discussions we've been having in the past few lectures. Our first approach will be **using units**: notice that the three constants that are present in the problem are α , m , and \hbar . If there's only one way to construct a quantity with units of energy using these constants, then all energy eigenvalues must be proportional to that quantity. When three constants have units that are not “linearly dependent,” that is indeed possible – we build objects with units of length, mass, or time, and then from that we can do anything. Because $\delta(x)$ has units of $\frac{1}{[L]}$ (remember that integrating the delta function over the real line gives us a unitless constant), and V has units of energy, we must have

$$[\alpha] = [E] \cdot [L] \implies \frac{[\alpha]}{[L]} = [E] = \frac{[\rho]^2}{[m]} = \frac{[\hbar]^2}{[m][L]^2},$$

so that $\frac{\hbar^2}{m\alpha}$ has units of length and thus our energy scale can be written as

$$[E] = \frac{[\alpha]}{[L]} = \frac{[m][\alpha]^2}{[\hbar]^2}.$$

This means that because the bound state energy must be in the forbidden region $E < 0$ throughout x , we therefore predict that

$$E_b = -\# \frac{m\alpha^2}{\hbar^2}$$

for some positive number $\#$, and there can't be any other possibilities just from our unit considerations! And we should expect that this number should not be particularly large or small – for the problem to be “natural,” we should expect $\#$ on the order of 1. But we'll be more precise about that in a second.

Another way we can think about this potential is to consider the **regularized** version of the delta function, which is basically a very deep and very narrow finite square well. Recall that because this is a symmetric potential (because there's nothing asymmetric about the delta function), the ground state should be even and have no nodes – refer to the pictures under Example 101 for illustration. But as the wavefunction in the classically allowed region becomes narrower and narrower, we expect the “curving back” in that region to occur more and more rapidly, so that in the limit we actually get a **discontinuity in the derivative** of the wavefunction ψ . With this, we can now write down the differential equation for the delta function potential (though we'll still not solve it): for $x \neq 0$, we have no potential,

so

$$-\frac{\hbar^2}{2m}\psi'' = E\psi \implies \psi'' = \kappa^2\psi \text{ for } x \neq 0,$$

where $\kappa^2 = -\frac{2mE}{\hbar^2} > 0$ just like in the finite square well. Such a differential equation has solutions $e^{\pm\kappa x}$ (as we already know), or equivalently $\cosh(\kappa x)$ and $\sinh(\kappa x)$ if we prefer. But we can think now about how many bound states this potential will have – if there's one of them, it will be even and have no nodes, and if there's a first excited state after that, it must be odd and vanish at the origin (so that it has one node). That occurs only with a function like $\psi(x) \propto \sinh(\kappa x)$, but that's not good because the function is **convex away from the axis** even in a forbidden region. So there can only be at most one bound state, and now we're ready to solve the problem algebraically. Because our ground state needs to be even, we must have

$$\boxed{\psi(x) = Ae^{-\kappa|x|} \text{ for } x \neq 0},$$

so that our function decays as $|x| \rightarrow \infty$, and this seems to be on the right track because it's what we expect from a ground state of the form in Example 101 with a very narrow middle region. Our wavefunction is indeed continuous, and now we just need to use the fact that the delta function is of intensity α . (It's good that our energy scale given in E_b has α in the numerator – indeed, as the potential gets stronger, the bound state should get deeper, so we have some reasonable conditions.) **This next part is important** because we'll do it again and again in this course: the Schrodinger equation with the potential term is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x),$$

and now we **integrate both sides** from $-\varepsilon$ to ε (where eventually we'll be looking at the limit $\varepsilon \rightarrow 0$) to get

$$-\frac{\hbar^2}{2m}\left(\frac{d\psi}{dx}\Big|_{x=\varepsilon} - \frac{d\psi}{dx}\Big|_{x=-\varepsilon}\right) + \int_{-\varepsilon}^{\varepsilon} -\alpha\delta(x)\psi(x)dx = E \int_{-\varepsilon}^{\varepsilon} \psi(x)dx,$$

because the integral of the second derivative is the first derivative. Now taking a limit, we have

$$-\frac{\hbar^2}{2m}\lim_{\varepsilon \rightarrow 0}\left(\frac{d\psi}{dx}\Big|_{x=\varepsilon} - \frac{d\psi}{dx}\Big|_{x=-\varepsilon}\right) - \alpha\psi(0) = \lim_{\varepsilon \rightarrow 0} E \int_{-\varepsilon}^{\varepsilon} \psi(x)dx = 0,$$

because ψ is not divergent and we're shrinking the limits of integration to a single point. Thus, rearranging this equation gives us what we wanted – we get the differences between the derivatives at 0^+ and 0^- , which allows us to see the discontinuity in ψ' , which we'll denote $\Delta_0\psi'$:

$$-\frac{\hbar^2}{2m}\Delta_0\psi' - \alpha\psi(0) = 0 \implies \boxed{\Delta_0\psi' = -\frac{2m\alpha}{\hbar^2}\psi(0)}.$$

In other words, as long as the wavefunction doesn't vanish, it can have a discontinuity due to a delta function, and in fact the change in derivative is proportional to the value of ψ and also to the strength of the delta function α . And returning to our wavefunction, notice that the derivative of our boxed $\psi(x)$ above has discontinuity

$$-\frac{2m\alpha}{\hbar^2}A = -\frac{2m\alpha}{\hbar^2}\psi(0) = \Delta_0\psi' = \lim_{\varepsilon \rightarrow 0}(-\kappa Ae^{-\kappa\varepsilon} - \kappa Ae^{-\kappa\varepsilon}) = -2\kappa A,$$

so that the $2A$ s cancel (we should not expect A to show up because it's just a normalizing factor in a linear equation), and we find $\boxed{\kappa = \frac{m\alpha}{\hbar^2}}$. And this is good, because we've now specified the energy of our bound state

$$E = -\frac{\hbar^2\kappa^2}{2m} = -\frac{\hbar^2}{2m}\frac{m^2\alpha^2}{\hbar^4} = \boxed{-\frac{m\alpha^2}{2\hbar^2}},$$

and indeed the number has been determined to be $n = \frac{1}{2}$. And with that, we've learned that a single delta function will give us a single bound state – adding more delta functions will give us more bound states, as we'll examine ourselves.

Example 105

We'll now spend a few minutes talking more about the **node theorem**, which we've stated and used for some of our previous arguments. We won't do a mathematically rigorous justification, but we'll give the main intuition for why we should believe it to be true.

Suppose we have bound energy eigenstates of a one-dimensional potential, labeled $\psi_1, \psi_2, \psi_3, \dots$ with respective energies E_1, E_2, E_3, \dots in increasing order. We are claiming that ψ_n has $(n - 1)$ nodes, and we'll understand this by thinking about **continuity**.

Fact 106

Note that the wavefunction can never have $\psi(x_0) = \psi'(x_0) = 0$, because for a second-order differential equation the initial conditions ψ and ψ' tell us everything and the general solution must be $\psi = 0$. So for any state ψ , **the derivative at a node must be nonzero**.

The idea is that if we have some arbitrary potential $V(x)$, we can truncate it to just the range $[-a, a]$ and get the **screened potential**

$$V_a(x) = \begin{cases} V(x) & |x| < a, \\ \infty & |x| > a. \end{cases}$$

In other words, we have an infinite well, but our potential is no longer flat inside the well. And as $a \rightarrow \infty$, the bound states of our screened potential will become the bound states of our original potential $V(x)$, because all bound states decay to 0 and thus the potential makes “less and less of an impact” as we move the walls outward. And as a increases, the bound states evolve continuously, but for small a we basically have a very narrow infinite well where the potential is essentially flat. Thus, as $a \rightarrow 0$, we can use the states of the infinite potential, in which we have a ground state with no nodes, a first excited state with one nodes, and so on, satisfying all of the assumptions of the node theorem. Thus, all that we need to show is that **as we increase the length of the screen, we cannot change the number of nodes continuously**.

Indeed, consider the derivative of the n th energy eigenstate of ψ_a at $x = a$. Introducing a new node as we increase a means that we go from approaching the boundary from below to above, or vice versa, meaning that ψ_a 's derivative at its endpoint must switch signs. Thus, there would need to be some intermediate value of a such that $\psi' = 0$ at the endpoint. But because we have an infinite wall at that point, we also have $\psi = 0$, and by Fact 106 this cannot occur for a nonzero wavefunction. Thus, no new nodes can be created. The same argument works for having a node disappear from our wavefunction, or having a node appear in the middle of the region (which would imply a tangent point when the node first emerges). So at least intuitively, we see that the n th energy eigenstate will continue to have $(n - 1)$ nodes as a gets larger, and thus in the limit we have the desired node theorem.

Our next step in this class is to look at a classical system that has a lot of deep theory, and we'll be returning to it in the next few lectures as well. Recall that classically, we have a system with a total potential plus kinetic energy

$$E = K + U = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2,$$

where $\omega = \sqrt{\frac{k}{m}}$ for the **spring constant** k (so that the potential term can also be written as $\frac{1}{2}kx^2$) and x represents the amount that a spring is stretched from its equilibrium position. To invent a quantum version of this system, we

must come up with a Hamiltonian for the Schrodinger equation, and we do this in the purest possible way:

Example 107 (Simple harmonic oscillator)

Consider a one-dimensional system with Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2,$$

where \hat{x} and \hat{p} are operators satisfying $[\hat{x}, \hat{p}] = i\hbar$.

It will turn out that the quantization of energies in this problem is pretty interesting – even though the classical oscillator can oscillate with any amplitude, this is not the case for the quantum oscillator. This Hamiltonian corresponds to the quadratic potential $V(x) = \frac{1}{2}mx^2$, and the reason it is so important is that it is a **good approximation for any potential around a local minimum** (since by Taylor expansion, the first derivative vanishes), meaning that the logic here can be (and in fact is) applied to many different oscillatory systems, like an electron in a magnetic field or the motion of a diatomic molecule.

There are two ways we can find the energy eigenstates of this oscillator – notice that because V is unbounded, **all energy eigenstates are bound states** for this system, which is not the case for something like the delta function potential. Our goal is to solve the equation $\hat{H}\phi_n(x) = E_n\phi_n(x)$ (where ϕ_n denotes the n th harmonic oscillator eigenstate), and we can do this either by **solving the differential equation directly** or by inventing certain clever **raising and lowering operators** which simplifies the problem to an algebraic trick. The latter of these will be covered more in 8.05, but we'll get a solution to the harmonic oscillator problem with both methods. First, we write down the equation

$$-\frac{\hbar^2}{2m} \frac{d^2\phi}{dx^2} + \frac{1}{2}m\omega^2x^2\phi(x) = E\phi(x),$$

and we'll first remove all of the units from the equation with a simple procedure: **change the variable x into one with no units**, which will simplify numerical simulation and also make the structure more illuminating. We do this by writing $x = au$ for a unitless u and a constant a with units of length; here, we can use m, ω, \hbar to define a via

$$[E] = \frac{[\hbar]^2}{[m][a]^2} = [m][\omega]^2[a]^2 \implies a^2 = \frac{\hbar}{m\omega}.$$

Plugging in $x = \sqrt{\frac{\hbar}{m\omega}}u$, we then get

$$-\frac{\hbar^2}{2ma^2} \frac{d^2\phi}{du^2} + \frac{1}{2}m\omega^2a^2u^2\phi = E\phi,$$

and now $m\omega^2a^2$ and $\frac{\hbar^2}{ma^2}$ have units of energy and must turn out to be something nice when we substitute in the actual value of a^2 : indeed, we end up with the equation

$$-\frac{1}{2}\hbar\omega \frac{d^2\phi}{du^2} + \frac{1}{2}\hbar\omega u^2\phi = E\phi.$$

And finally, the equation looks nicest if we multiply by $\frac{2}{\hbar\omega}$ to get

$$-\frac{d^2\phi}{du^2} + u^2\phi = \frac{2E}{\hbar\omega}\phi = \mathcal{E}\phi,$$

where $\mathcal{E} = \frac{2E}{\hbar\omega}$ is the unit-free energy. Since knowing E and \mathcal{E} are equivalent, we'll find that working with \mathcal{E} gives us

the nicest answer: we're essentially left with solving the second-order differential equation

$$\boxed{\frac{d^2\phi}{du^2} = (u^2 - \mathcal{E})\phi.}$$

Thinking back to the "shooting method" from last lecture, this equation will have solutions for all values of \mathcal{E} , but most of them will diverge and not be normalizable. To understand this, we'll consider the system for large x (that is, large u) and see what the solution must look like there. Since \mathcal{E} is a constant, the **limiting behavior** of the differential equation looks like $\frac{d^2\phi}{du^2} = u^2\phi$. The way to get this kind of solution (where we gain powers of u after differentiating) is not by using polynomials in u but by trying expressions of the form

$$\phi(u) = u^k e^{\frac{\alpha u^2}{2}}.$$

Indeed, we find that because we're just trying to get a rough order of approximation, we have $\phi' \sim \alpha u\phi$ (the other term is comparably negligible) and thus $\phi'' = (\alpha u)^2\phi +$ (subleading terms). Thus, setting $\alpha = \pm 1$ are likely to give us approximate solutions, because those get us back to the original differential equation. Going further, we thus expect that our large- $|u|$ behavior will look like

$$\phi(u) \sim Au^k e^{-u^2/2} + Bu^k e^{u^2/2},$$

and now we can see where we might run into trouble: we can't have the second of these two terms, so we must have \mathcal{E} chosen so that $B = 0$ is the desired solution. (And remember that everything here so far is still $|u| \rightarrow \infty$, so we don't have any exact solutions, only general behavior for large u .)

So **without any loss of generality**, we'll write

$$\phi(u) = h(u)e^{-u^2/2};$$

we can always multiply back by $e^{u^2/2}$ to get to the original function, but this should encode some of the limiting behavior that we expect, and we hope that $h(u)$ will not diverge too quickly (because then $\phi(u)$ will be normalizable) – specifically, now that we've isolated the divergence, we hope to see that $h(u)$ is actually a polynomial, because then it is easier to see "when our solution ends." Our next step is then to get the differential equation for $h(u)$; it will turn out that we must solve

$$\boxed{\frac{d^2h}{du^2} - 2u\frac{dh}{du} + (\mathcal{E} - 1)h = 0.}$$

Next time, we'll dive more into this and understand how quantization helps us get to the final answer!

Lecture 14: Eigenstates of the Harmonic Oscillator

Last time, we took our harmonic oscillator Hamiltonian and simplified it to an equation with a unit-free coordinate u and a unit-free energy \mathcal{E} , giving us the differential equation $\frac{d^2\phi}{du^2} = (u^2 - \mathcal{E})\phi$. We then analyzed the large- $|u|$ behavior of ϕ , and after making the definition $\phi(u) = h(u)e^{-u^2/2}$ (to isolate the most serious divergence of ϕ), we arrived at a new differential equation $\frac{d^2h}{du^2} - 2u\frac{dh}{du} + (\mathcal{E} - 1)h = 0$, which we'll work towards solving today.

To start, we'll attempt a series expansion of the form

$$h(u) = \sum_{k=0}^{\infty} a_k u^k.$$

We can proceed by directly plugging this into the differential equation, but that involves reindexing sums and can be a bit complicated. Instead, we can just consider the terms with u^j 's: we must start with a u^{j+2} in the first term, a u^j in the second term, and a u^j in the third term, so we find that for all $j \geq 0$, we require

$$(j+2)(j+1)a_{j+2}u^j - 2ja_ju^j + (\mathcal{E}-1)a_ju^j = 0 \implies (j+2)(j+1)a_{j+2} - 2ja_j + (\mathcal{E}-1)a_j = 0.$$

(Specifically, we're using the fact that a power series of u can only be identically zero if each term in $\sum a_j u^j$ is zero.) In other words, the coefficients of our power series must be related as

$$(j+2)(j+1)a_{j+2} = (2j+1-\mathcal{E})a_j \implies a_{j+2} = \frac{2j+1-\mathcal{E}}{(j+2)(j+1)}a_j,$$

giving us a recurrence relation for the a_j s. So now we can start with a_0 and successively obtain a_2, a_4, a_6 , and so on, which gives us an **even** solution $h(u)$, or we can start with a_1 and successively obtain a_3, a_5, a_7 , and so on, giving us an **odd** solution. (Notice that specifying a_0 and a_1 is just like specifying the value of $h(u)$ and $h'(u)$ at $u=0$, so it makes sense that those two values are all we need to get the full solution of the differential equation.)

But now we must ask what happens to these coefficients a_j , because as written the solution may go on forever. Then we have

$$\frac{a_{j+2}}{a_j} = \frac{2j+1-\mathcal{E}}{(j+2)(j+1)} \sim \frac{2j}{j^2} = \frac{2}{j},$$

so the coefficients do decay. But they aren't decaying fast enough – notice that for example that

$$e^{u^2} = \sum_{n=0}^{\infty} \frac{1}{n!} u^{2n}.$$

Looking at the even $j=2n$, we have terms of the form $\frac{1}{(j/2)!} u^j$, so the coefficients $c_j = \frac{1}{(j/2)!}$ satisfy $\frac{c_{j+2}}{c_j} = \frac{1}{\frac{j+2}{2}} = \frac{2}{j+2} \sim \frac{2}{j}$ (no issues with fractional factorials because j is even). So the point is that if we don't truncate the recursion relation at some point, our wavefunction will actually be unbounded, because $h(u) \sim e^{u^2}$, meaning that $\phi(u) \sim e^{u^2/2}$ (the "safety factor" isn't enough to make our normalization work). So the differential equation cannot work with arbitrary energies – **the normalization requirement now quantizes the energies for us**, because the only way we can make this work is to have $\frac{a_{j+2}}{a_j} = 0$ for some j , meaning that

$$\boxed{\mathcal{E} = 2j + 1 \text{ for some } j \in \mathbb{Z}_{\geq 0}},$$

and for whichever value of j that is picked, we will have $a_{j+2} = 0$ (because the numerator in the recurrence is then 0). Even for $j=0$, we'll have a nonzero a_0 but not a_2 , and that gives us a nontrivial wavefunction as well. So putting everything together, our wavefunctions are of the form

$$h(u) = a_n u^n + a_{n-2} u^{n-2} + a_{n-4} u^{n-4} + \dots$$

for some nonnegative integer n (an even function for even n and an odd function for odd n – remember that energy eigenstates must always be either even or odd), and those correspond to energies of $\mathcal{E} = 2n + 1$ and thus an energy of

$E = \frac{\hbar\omega}{2}(2n+1) = \hbar\omega \left(n + \frac{1}{2} \right)$. So we've arrived at a famous fact: the energy levels of a harmonic oscillator are evenly spaced, except there is an offset of $\frac{1}{2}\hbar\omega$ so that the ground state is already a little above $E=0$.

Definition 108

The **Hermite polynomial** $H_n(u)$ is the polynomial satisfying the **Hermite differential equation**

$$\frac{d^2}{du^2} H_n(u) - 2u \frac{dH_n}{du} + 2nH_n(u) = 0,$$

with normalization chosen so that $H_n(u)$ has leading term $2^n u^n$.

(We know that the leading term is of degree n , and because the Hermite differential equation is linear, we can always scale as we wish.) A few small cases that we can keep in mind are

$$H_0(u) = 1, \quad H_1(u) = 2u, \quad H_2(u) = 4u^2 - 2, \quad H_3(u) = 8u^3 - 12u.$$

It turns out that we have the generating functional

$$e^{-z^2+2zu} = \sum_{n=0}^{\infty} \frac{z^n}{n!} H_n(u)$$

which we can use to compute Hermite polynomials by expanding out the left-hand side and collecting terms by powers of z . And with this formula, we can indeed see that $H_n(u)$ begins with $2^n u^n$, and showing that these z -coefficients indeed satisfy the Hermite differential equation turns out to be pretty simple as well.

But turning back to our original problem, we can substitute $\frac{x}{a}$ back in for u , so that we can see the form of our original wavefunctions: we have

$$\phi_n(x) = N_n H_n\left(\frac{x}{a}\right) e^{-\frac{x^2}{2a^2}}, \quad a^2 = \frac{\hbar}{m\omega}$$

for some normalization constant N_n , with corresponding energies

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

We'll now turn to an **operator-based algebraic approach**: if we look back at the simple harmonic oscillator Hamiltonian again, we can write it as a sum of squares

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2 = \frac{1}{2} m\omega^2 \left(\hat{x}^2 + \frac{\hat{p}^2}{m^2\omega^2} \right).$$

We'll now try to factorize the Hamiltonian essentially as the product of two factors: we wish to write $\hat{H} = \hat{V}^\dagger \hat{V} + c$, where \hat{V}^\dagger is the Hermitian conjugate of \hat{V} . In particular, adding the constant c only shifts our energies without doing anything important, and then writing as $\hat{V}^\dagger \hat{V}$ ensures that \hat{H} is still Hermitian (because $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger$, and $(\hat{V}^\dagger)^\dagger = \hat{V}$). We'll soon see why this is a useful thing to do, but first we'll see how to actually factor in this case: if we had $a^2 - b^2$, then we could factor as $(a - b)(a + b)$, and now because we have $a^2 + b^2$, it makes sense to factor as $(a + ib)(a - ib)$ instead. Since quantum mechanics inherently needs complex numbers, this is a reasonable thing to try: we in fact almost have

$$\hat{x}^2 + \frac{\hat{p}^2}{m^2\omega^2} \stackrel{?}{=} \left(\hat{x} - i \frac{\hat{p}}{m\omega} \right) \left(\hat{x} + i \frac{\hat{p}}{m\omega} \right),$$

but this is not exactly true because we have operators instead of numbers, so commutativity matters: indeed, we instead have

$$\left(\hat{x} - i \frac{\hat{p}}{m\omega} \right) \left(\hat{x} + i \frac{\hat{p}}{m\omega} \right) = \hat{x}^2 + \frac{\hat{p}^2}{m^2\omega^2} + \frac{i}{m\omega} [\hat{x}, \hat{p}].$$

Since the commutator here is $i\hbar$, the constant term is $-\frac{\hbar}{m\omega}$, so we instead have that

$$\hat{x}^2 + \frac{\hat{p}^2}{m^2\omega^2} = \left(\hat{x} - i\frac{\hat{p}}{m\omega} \right) \left(\hat{x} + i\frac{\hat{p}}{m\omega} \right) + \frac{\hbar}{m\omega} I,$$

where I denotes the identity operator. But now we can call the two terms in parentheses \hat{V}^\dagger and \hat{V} , respectively – more specifically, we can define $\hat{V} = \hat{x} + i\frac{\hat{p}}{m\omega}$ and notice that \hat{V}^\dagger is indeed the other term, because \hat{x} and \hat{p} are each their own Hermitian conjugate and the i turns into a $-i$. So putting everything together and simplifying, our Hamiltonian is now

$$\hat{H} = \frac{1}{2}m\omega^2\hat{V}^\dagger\hat{V} + \frac{1}{2}\hbar\omega.$$

However, \hat{V} and \hat{V}^\dagger still have units here, so we'll simplify a bit more. We can do this by computing the commutator

$$[\hat{V}, \hat{V}^\dagger] = \left[\hat{x} + \frac{i\hat{p}}{m\omega}, \hat{x} - \frac{i\hat{p}}{m\omega} \right].$$

The terms of the same type commute, so we're left with

$$= -\frac{i}{m\omega}[\hat{x}, \hat{p}] + \frac{i}{m\omega}[\hat{p}, \hat{x}] = \frac{\hbar}{m\omega} + \frac{\hbar}{m\omega} = \frac{2\hbar}{m\omega}.$$

Thus, we can renormalize to find

$$\left[\sqrt{\frac{m\omega}{2\hbar}}\hat{V}, \sqrt{\frac{m\omega}{2\hbar}}\hat{V}^\dagger \right] = I,$$

and because these normalized operators are nice we'll give them special names (which will make sense soon):

Definition 109

The **destruction operator** (also **annihilation operator**) \hat{a} and **creation operator** \hat{a}^\dagger are given by

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\hat{V}, \quad \hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\hat{V}^\dagger,$$

where $\hat{V} = \hat{x} + i\frac{\hat{p}}{m\omega}$.

We can verify that \hat{a} and \hat{a}^\dagger are unit-free, because we have $[\hat{a}, \hat{a}^\dagger] = 1$. (And because \hat{a}^\dagger is different from \hat{a} , this is not a Hermitian operator.) Since we're defining \hat{a} and \hat{a}^\dagger in terms of \hat{x} and \hat{p} , we can also get the equations the other way around, which are

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a} + \hat{a}^\dagger), \quad \hat{p} = i\sqrt{\frac{m\omega\hbar}{2}}(\hat{a}^\dagger - \hat{a}).$$

Notice that from these expressions, it's consistent that \hat{x} and \hat{p} are Hermitian (taking the conjugates of the right-hand sides just swap the roles of \hat{a} and \hat{a}^\dagger , and the i in \hat{p} 's expression becomes a $-i$, giving us the original expression again). So now we can write our Hamiltonian in terms of \hat{a} and \hat{a}^\dagger instead of \hat{x} and \hat{p} , since that was the original goal: we know that

$$\hat{V}^\dagger\hat{V} = \frac{2\hbar}{m\omega}\hat{a}^\dagger\hat{a} \implies \hat{H} = \hbar\omega \left(\hat{a}^\dagger\hat{a} + \frac{1}{2} \right).$$

So we've now factorized \hat{H} using these creation and destruction operators, and now it turns out we'll be able to solve the harmonic oscillator while barely needing to solve any differential equations (we just need to solve a single first-order differential equation)! Recall that we have the inner product

$$(\phi, \psi) = \int \phi^*(x)\psi(x)dx,$$

so the expectation value of the Hamiltonian in a state ψ is

$$\langle H \rangle_\psi = (\psi, \hat{H}\psi) = \left(\psi, \hbar\omega \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right) \psi \right) = \hbar\omega (\psi, \hat{a}^\dagger \hat{a} \psi) + \frac{\hbar\omega}{2} (\psi, \psi).$$

Because ψ is normalized, the second inner product is 1, and now by the definition of a Hermitian conjugate, we can move the \hat{a}^\dagger operator to the other side:

$$= \hbar\omega (a\psi, a\psi) + \frac{\hbar\omega}{2}.$$

Now $(a\psi, a\psi) \geq 0$ for any state ψ (because plugging this into the definition of the integral gives us the integral of a nonnegative quantity). Thus, we find that $\langle H \rangle_\psi \geq 0 + \frac{\hbar\omega}{2}$, and this is the advantage of writing the Hamiltonian as $\hat{V}^\dagger \hat{V}$: this flipping argument tells us that we always get energies bounded from below.

So now for **any** energy eigenstate ψ , $\langle H \rangle_\psi \geq \frac{\hbar\omega}{2}$, meaning that **any** energy eigenvalue is at least $\frac{\hbar\omega}{2}$. We know (from our previous method) that there is in fact an energy eigenstate of energy exactly $\frac{\hbar\omega}{2}$, and the way we arrive at that fact is by noting that we get equality **only if** $(\hat{a}\psi, \hat{a}\psi) = 0 \implies \hat{a}\psi = 0$. Thus, if there is a ground state ψ_0 , it must satisfy

$$\hat{a}\psi_0 = 0 \implies \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} + i \frac{\hat{p}}{m\omega} \right) \psi_0 = 0,$$

by plugging in our definition of \hat{a} . Removing the constant and converting everything to x -coordinates gives us the differential equation

$$\left(x + \frac{\hbar}{m\omega} \frac{d}{dx} \right) \psi_0(x) = 0,$$

and we've turned our second-order differential equation into a first-order differential equation by exploiting Hermiticity! This differential equation is much easier to solve – we have

$$\frac{d\psi_0}{dx} = -\frac{m\omega}{\hbar} x \psi_0 \implies \boxed{\psi_0(x) = N_0 e^{-\frac{m\omega}{2\hbar} x^2}},$$

which is normalized when $N_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$. So our ground state is a perfect Gaussian, and we can indeed check that

$$\hat{H}\psi_0 = \hbar\omega \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right) \psi_0 = \frac{\hbar\omega}{2} \psi_0,$$

because \hat{a} acting on ψ_0 already makes that term 0, and we recover the correct ground state energy for the harmonic oscillator.

We'll continue this discussion next time, since we still need to find all of the excited states. But basically, it turns out $\hat{a}^\dagger \hat{a}$ is an important Hermitian operator called the **number operator**, and then using the fact that $\hat{a}\hat{a}^\dagger - \hat{a}^\dagger \hat{a} = 1$ allows us to "create" new energy eigenstates with the creation operator \hat{a}^\dagger . We'll essentially see that $\psi_0, \hat{a}^\dagger \psi_0, \hat{a}^\dagger \hat{a}^\dagger \psi_0, \dots$ give us the full set of excited states for the harmonic oscillator!

Lecture 15: Excited Harmonic Oscillator States and Scattering States

Last time, we did an algebraic analysis where we factored the harmonic oscillator Hamiltonian in the form

$$\hat{H} = \hbar\omega \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right),$$

which allowed us to see that any energy eigenstate has energy at least $\frac{\hbar\omega}{2}$ and also allowed us to find the unique ground state ψ_0 using a first-order differential equation. (Recall that \hat{a} is a linear combination of \hat{x} and \hat{p} , such that $[\hat{a}, \hat{a}^\dagger] = 1$.) And we do expect to see a nondegenerate ground state, because there are no degeneracies in the bound state spectrum of a one-dimensional potential.

Definition 110

The **number operator** \hat{N} for the harmonic oscillator is $\hat{N} = \hat{a}^\dagger \hat{a}$.

We can check that \hat{N} is Hermitian (because the conjugate of a product is the product of the conjugates, but in reverse order) and that $\hat{N}\phi_0 = 0$ (because $\hat{N}\phi_0 = \hat{a}^\dagger(\hat{a}\phi_0) = \hat{a}^\dagger 0 = 0$). In particular, \hat{N} is basically the Hamiltonian up to a linear shift, and it's unitless because \hat{a} and \hat{a}^\dagger are, so it'll be a useful thing to work with (as a dimensionless energy). Specifically, eigenstates of \hat{N} and \hat{H} are the same, with $E = \hbar\omega(N + \frac{1}{2})$.

Today, we'll explore how to use this number operator to get excited states of the harmonic oscillator, completing our solution. We'll first understand how it interacts with the other operators we have here, and this often means computing relevant commutators. We have that

$$[\hat{N}, \hat{a}] = [\hat{a}^\dagger \hat{a}, \hat{a}] = [\hat{a}^\dagger, \hat{a}] \hat{a} = -\hat{a}$$

(because the \hat{a} commutes with the \hat{a}), which is a simple expression, and similarly

$$[\hat{N}, \hat{a}^\dagger] = [\hat{a}^\dagger \hat{a}, \hat{a}^\dagger] = \hat{a}^\dagger [\hat{a}, \hat{a}^\dagger] = \hat{a}^\dagger.$$

So the commutator of \hat{N} with either \hat{a} or \hat{a}^\dagger gives back a number times either of those two operators, and those numbers are why \hat{a} , the destruction operator, is also called the **lowering operator** and why \hat{a}^\dagger is similarly called the **raising operator**. We can also additionally compute (if we're confused about what's going on here, we should try some small values of k to have a clear picture)

$$[\hat{a}, (\hat{a}^\dagger)^k] = k(\hat{a}^\dagger)^{k-1}.$$

because we essentially have to move an \hat{a} across a string of k \hat{a}^\dagger s, and each time we move once we gain a contribution of $(\hat{a}^\dagger)^{k-1}[\hat{a}, \hat{a}^\dagger] = (\hat{a}^\dagger)^{k-1}$. This should remind us of the commutators $[\hat{p}, \hat{x}^n]$ from earlier in the course as well.

Example 111

Taking a look at the $k = 2$ case,

$$[\hat{a}, (\hat{a}^\dagger)^2] = \hat{a}\hat{a}^\dagger\hat{a}^\dagger - \hat{a}^\dagger\hat{a}^\dagger\hat{a} = (\hat{a}\hat{a}^\dagger\hat{a}^\dagger - \hat{a}^\dagger\hat{a}\hat{a}^\dagger) + (\hat{a}^\dagger\hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a}^\dagger\hat{a}),$$

and each of these terms simplifies to \hat{a}^\dagger :

$$= ([\hat{a}, \hat{a}^\dagger]\hat{a}^\dagger) + (\hat{a}^\dagger[\hat{a}, \hat{a}^\dagger]) = \hat{a}^\dagger + \hat{a}^\dagger = 2\hat{a}^\dagger.$$

Similarly, we also have a commutator of the form

$$[\hat{a}^\dagger, (\hat{a})^k] = -k\hat{a}^{k-1},$$

so using these results, we find that we can do more with the number operator: we have

$$[\hat{N}, (\hat{a})^k] = -k(\hat{a})^k$$

by basically taking the equation in the line above and putting an extra \hat{a} in the left argument of the commutator (which commutes with the right argument), and similarly

$$[\hat{N}, (\hat{a}^\dagger)^k] = k(\hat{a}^\dagger)^k.$$

So even with a string of \hat{a} s or \hat{a}^\dagger s, taking the commutator with \hat{N} still gives us back the same operator with a number, and in fact that counts the number of \hat{a} s or \hat{a}^\dagger s – this explains the reason for the name **number operator**.

We'll now see how this all comes together – define the state

$$\phi_1 = \hat{a}^\dagger \phi_0.$$

(Remember that $\hat{a}\phi_0 = 0$, so we wouldn't get an interesting quantum state if we tried applying the other operator.) We may ask if this is an energy eigenstate, and the easiest way to check this is to see if it's a number eigenstate. Indeed, a useful manipulation is to say that

$$\hat{N}\phi_1 = \hat{N}\hat{a}^\dagger\phi_0 = [\hat{N}, \hat{a}^\dagger]\phi_0,$$

since \hat{N} kills ϕ_0 , so the $\hat{a}^\dagger\hat{N}\phi_0$ term is zero. And the formulas for commutators we've established above means that it's often easier to work with them than products – since $[\hat{N}, \hat{a}^\dagger] = \hat{a}^\dagger$, we find that

$$\hat{N}\phi_1 = \hat{a}^\dagger\phi_0 = \phi_1,$$

meaning that ϕ_1 is an eigenstate of \hat{N} (and thus \hat{H}) of eigenvalue 1 (and thus $\hbar\omega(1 + \frac{1}{2}) = \frac{3}{2}\hbar\omega$). And this is the reason for the name “creation operator” – acting on the vacuum (lowest energy state) with \hat{a}^\dagger gives us a new eigenstate. And if we want a more concrete expression for the wavefunction, we can write \hat{a}^\dagger and ϕ_0 in terms of x or p and get an explicit formula.

We defined ϕ_0 to be a normalized energy eigenstate, and it makes sense to ask whether ϕ_1 is normalized. This might seem like it is even more difficult than normalizing ϕ_0 , but in fact most of the work has already been done:

$$(\phi_1, \phi_1) = (\hat{a}^\dagger\phi_0, \hat{a}^\dagger\phi_0) = (\phi_0, \hat{a}\hat{a}^\dagger\phi_0) = (\phi_0, [\hat{a}, \hat{a}^\dagger]\phi_0) = (\phi_0, \phi_0) = 1$$

by the properties of the Hermitian conjugate and a similar commutator manipulation as above. (And learning how to do these kinds of algebraic tricks just comes with practice.)

To get the next state, we'll try to define the state

$$\phi'_2 = \hat{a}^\dagger\hat{a}^\dagger\phi_0.$$

Like before, we can check if we have an energy eigenstate by noting that

$$\hat{N}\phi'_2 = \hat{N}(\hat{a}^\dagger)^2\phi_0 = [\hat{N}, (\hat{a}^\dagger)^2]\phi_0 = 2(\hat{a}^\dagger)^2\phi_0 = 2\phi'_2,$$

so we have an energy eigenstate of energy $\hbar\omega(2 + \frac{1}{2}) = \frac{5}{2}\hbar\omega$. This time when checking normalization, we find that

$$(\phi'_2, \phi'_2) = (\hat{a}^\dagger\hat{a}^\dagger\phi_0, \hat{a}^\dagger\hat{a}^\dagger\phi_0) = (\phi_0, \hat{a}\hat{a}\hat{a}^\dagger\hat{a}^\dagger\phi_0).$$

Now the blue \hat{a} would kill ϕ_0 , so we can substitute in a commutator with the subsequent \hat{a}^\dagger s:

$$= (\phi_0, \hat{a}[\hat{a}, (\hat{a}^\dagger)^2]\phi_0) = (\phi_0, \hat{a} \cdot 2\hat{a}^\dagger\phi_0).$$

Pulling out the 2 and then using the same commutator trick as before gives us

$$= 2(\phi_0, [\hat{a}, \hat{a}^\dagger]\phi_0) = 2,$$

so this time our energy eigenstate needs to be defined as

$$\phi_2 = \frac{1}{\sqrt{2}} \hat{a}^\dagger \hat{a}^\dagger \phi_0.$$

We can now generalize these calculations:

Proposition 112

The n th excited state of the simple harmonic oscillator is

$$\phi_n = \frac{1}{\sqrt{n!}} (\hat{a}^\dagger)^n \phi_0.$$

This state has number eigenvalue n and thus energy eigenvalue $\hbar\omega (n + \frac{1}{2})$.

These calculations can be checked by noting (for the number operator) that

$$\hat{N}\phi_n = \frac{1}{\sqrt{n!}} \hat{N}(\hat{a}^\dagger)^n \phi_0 = \frac{1}{\sqrt{n!}} [\hat{N}, (\hat{a}^\dagger)^n] \phi_0 = \frac{1}{\sqrt{n!}} n(\hat{a}^\dagger)^n \phi_0 = n\phi_n,$$

and (for the normalization) that

$$(\phi_n, \phi_n) = \frac{1}{n!} (\phi_0, \hat{a}^n (\hat{a}^\dagger)^n) = \frac{1}{n!} (\phi_0, \hat{a}^{n-1} [\hat{a}, (\hat{a}^\dagger)^n] \phi_0) = \frac{1}{n!} (\phi_0, \hat{a}^{n-1} \cdot n(\hat{a}^\dagger)^{n-1} \phi_0)$$

and then inductively pulling out factors of $(n-1), (n-2), \dots, 2, 1$ to cancel out with the $\frac{1}{n!}$.

With this structure in place, we can notice that applying \hat{a}^\dagger to any of the energy eigenstates gets us the next higher energy eigenstate (with some constant factor). On the other hand, applying \hat{a} to an energy eigenstate gets us the next lower energy eigenstate, because it essentially cancels out one of the \hat{a}^\dagger s. To be more precise, notice that

$$\boxed{\hat{a}\phi_n} = \frac{1}{\sqrt{n!}} \hat{a} (\hat{a}^\dagger)^n \phi_0 = \frac{1}{\sqrt{n!}} [\hat{a}, (\hat{a}^\dagger)^n] \phi_0 = \frac{1}{\sqrt{n!}} n(\hat{a}^\dagger)^{n-1} \phi_0 = \frac{1}{\sqrt{n!}} n\sqrt{(n-1)!} \phi_{n-1} = \frac{n}{\sqrt{n}} \phi_{n-1} = \boxed{\sqrt{n}\phi_{n-1}},$$

and similarly we have the relation

$$\boxed{\hat{a}^\dagger\phi_n} = \frac{1}{\sqrt{n!}} (\hat{a}^\dagger)^{n+1} \phi_0 = \frac{1}{\sqrt{n!}} \sqrt{(n+1)!} \phi_{n+1} = \boxed{\sqrt{n+1}\phi_{n+1}}.$$

This gives us all of the tools we might need to do calculations like the following:

Example 113

Suppose we want to calculate the expectation values $\langle \hat{x} \rangle_{\phi_n}$ and $\langle \hat{p} \rangle_{\phi_n}$ in our energy eigenstates.

In our conventional language, this is difficult to compute, because we would need to write ϕ_n in terms of a Hermite polynomial and then take a complicated integral. But there are very quick alternative calculations to get us the answer:

- For the expectation value of \hat{x} , we are essentially calculating an expression like $\int x(\phi_n(x))^2 dx$. But because we have a symmetric potential, all of the $\phi_n(x)$ s are either even or odd, so their squares are always even. Thus the integrand is odd and the expectation is always zero.
- For the expectation value of \hat{p} , because we have a stationary state, it doesn't make sense to have a nonzero

momentum because “the state doesn’t move.” (And this is actually a more general result: the expectation of the momentum on a bound state with a real wavefunction is always zero, by integration by parts.)

But in preparation for more complicated calculations, we can also write out these expectations in terms of raising and lowering operators:

$$\langle \hat{x} \rangle_{\phi_n} = 0 = (\phi_n, \hat{x} \phi_n) = \sqrt{\frac{\hbar}{2m\omega}} (\phi_n, (\hat{a} + \hat{a}^\dagger) \phi_n).$$

But now $(\hat{a} + \hat{a}^\dagger)\phi_n$ is a linear combination of ϕ_{n-1} and ϕ_{n+1} (specifically, it is $\sqrt{n}\phi_{n-1} + \sqrt{n+1}\phi_{n+1}$), and the overlap of this with ϕ_n is zero **by orthogonality of the energy eigenstates** (because they have different energy eigenvalues). Another way to understand this orthogonality in the harmonic oscillator case is that if we wanted to compute something like

$$(\phi_3, \phi_2) = (\hat{a}^\dagger \hat{a}^\dagger \hat{a}^\dagger \phi_0, \hat{a}^\dagger \hat{a}^\dagger \phi_0) = (\phi_0, \hat{a} \hat{a} \hat{a} \hat{a}^\dagger \phi_0),$$

there are too many \hat{a} s – two of them can cancel out with the \hat{a}^\dagger s, but the last one will kill ϕ_0 , and this will always vanish. So whenever $m \neq n$, (ϕ_m, ϕ_n) will indeed be zero.

Example 114

Suppose that we now want to calculate the uncertainty Δx in ϕ_n , meaning that we must calculate $(\Delta x)^2 = \langle \hat{x}^2 \rangle_{\phi_n} - (\langle \hat{x} \rangle_{\phi_n})^2 = \langle \hat{x}^2 \rangle_{\phi_n}$.

This time, we will need the full power of the creation and annihilation operators (because doing the integral with Hermite polynomials would require a lot of work or creativity): we find that

$$\langle \hat{x}^2 \rangle_{\phi_n} = (\phi_n, \hat{x}^2 \phi_n) = \frac{\hbar}{2m\omega} (\phi_n, (\hat{a} + \hat{a}^\dagger)(\hat{a} + \hat{a}^\dagger) \phi_n).$$

Expanding out (what we really care about is the ϕ_n coefficient in the second argument), we have

$$= \frac{\hbar}{2m\omega} (\phi_n, (\hat{a}\hat{a} + \hat{a}^\dagger\hat{a}^\dagger + \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a})\phi_n)$$

and now only the last two of the four terms give us a nonzero contribution by orthogonality, so we can use the boxed relations (of \hat{a} and \hat{a}^\dagger acting on ϕ_n) above to get

$$= \frac{\hbar}{2m\omega} (\phi_n, (\sqrt{n+1} \cdot \sqrt{n+1} + \sqrt{n} \cdot \sqrt{n})\phi_n) = \frac{\hbar}{2m\omega} (2n+1),$$

or we can rewrite in terms of the number operator, using that $\hat{a}\hat{a}^\dagger = [\hat{a}, \hat{a}^\dagger] + \hat{a}^\dagger\hat{a} = 1 + \hat{N}$, to find again that the squared uncertainty is

$$\boxed{\langle \hat{x}^2 \rangle_{\phi_n}} = \frac{\hbar}{2m\omega} (\phi_n, (2\hat{N} + 1)\phi_n) = \boxed{\frac{\hbar}{2m\omega} (2n+1)}.$$

And similarly, we can calculate the uncertainty Δp , giving us an explicit calculation of $\Delta x \Delta p$ for this state – this is left as an exercise to us.

With that, we’ll now turn to a new topic:

Definition 115

Scattering states are energy eigenstates that cannot be normalized.

The motivating examples to keep in mind here are the $e^{ipx/\hbar}$ infinite plane wave solutions – even though they individually cannot be normalized, they can be put together to create (normalizable) wave packets, which can properly represent particles. We’ll start with a particularly illustrative example, the **step potential**:

Example 116 (Step potential)

Consider a one-dimensional system given by the potential

$$V(x) = \begin{cases} 0 & x < 0, \\ V_0 & x \geq 0. \end{cases}$$

Recalling that energy eigenstates must have energy at least $\min V(x)$, we know that any eigenstate will have positive energy, and thus there are two qualitative cases, namely $E < V_0$ and $E > V_0$. But it turns out we can just solve one of the two cases and “do the other by analytic continuation” – no matter which case we’re in, the solution will be non-decaying for $x < 0$ (because $E > V$), and thus energy eigenstates will never be normalizable.

We’ll first do the case where $E > V_0$ (so that the solution is sinusoidal for both $x > 0$ and $x < 0$), and we’ll visualize a solution as “coming in from the left:”

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0, \\ Ce^{i\bar{k}x} & x \geq 0. \end{cases}$$

This is a wave “coming in from the left” because putting in the $e^{-iEt/\hbar}$ factor into Ae^{ikx} gives us an $e^{i(kx-\omega t)}$ traveling wave. Analogously to the systems studied in 8.03, this wave will then have a “reflected” and a “transmitted” component, corresponding to the Be^{-ikx} and $Ce^{i\bar{k}x}$ parts, respectively. And we know what k and \bar{k} must be from the Schrodinger equation: since the kinetic energy of the particle is $\frac{\hbar^2 k^2}{2m}$, we must have $k^2 = \frac{2mE}{\hbar^2}$ and $\bar{k}^2 = \frac{2m(E - V_0)}{\hbar^2}$. Furthermore, the wavefunction and its derivative must be continuous at $x = 0$ (since there are no delta functions), so

$$A + B = C, \quad ikA - ikB = i\bar{k}C \implies A - B = \frac{\bar{k}}{k}C.$$

So there will be one free parameter among A, B, C , which is okay because A is the “input” strength of the incoming wave – what matters is the values $\frac{B}{A} = \frac{k - \bar{k}}{k + \bar{k}}$ and $\frac{C}{A} = \frac{2k}{k + \bar{k}}$. And we’ll see next time how to turn this into a wave packet for a physical particle!

Lecture 16: Reflection and Transmission

Last lecture, we began our study of scattering states (energy eigenstates that are not normalizable). Specifically, we constructed the energy eigenstates for the step potential (jumping from 0 to V_0 at $x = 0$), which we can interpret as an incoming plane wave with a reflected and transmitted component (copied from last lecture):

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0, \\ Ce^{i\bar{k}x} & x \geq 0. \end{cases}$$

The relevant ratios for reflection and transmission in this potential turn out to be

$$\frac{B}{A} = \frac{k - \bar{k}}{k + \bar{k}}, \quad \frac{C}{A} = \frac{2k}{k + \bar{k}}, \quad \text{where } k^2 = \frac{2mE}{\hbar^2}, \quad \bar{k}^2 = \frac{2m(E - V_0)}{\hbar^2}$$

(since the particle has different kinetic energies in the two parts of the potential and thus different de Broglie wavelengths). And if we now look at the limit where $E \rightarrow V_0$, we find that $\bar{k} \rightarrow 0$ and thus $B \rightarrow A$ and $C \rightarrow 2A$, yielding

the solution

$$\psi(x) = \begin{cases} 2A \cos kx & x < 0, \\ 2A & x \geq 0. \end{cases}$$

(This isn't normalizable, but neither is the original solution, so we don't need to worry too much about that.)

We can now discuss the **conservation of probability** principle from earlier in the course. We can imagine a probability current flowing into the step potential from the left, and if we imagine a narrow window around the discontinuity, we must have the same amount of probability current leaving that window as entering: recall that

$$J(x) = \frac{\hbar}{m} \text{Im} \left(\psi^* \frac{\partial \psi}{\partial x} \right),$$

so for our $E = V_0$ state we have, for $x < 0$ and $x > 0$ respectively,

$$J_L(x) = \frac{\hbar k}{m} (|A|^2 - |B|^2), \quad J_R(x) = \frac{\hbar \bar{k}}{m} |C|^2.$$

Indeed, we see that the current doesn't depend on the value of x and is (after some computation) equal for $x < 0$ and $x > 0$ (keep in mind that all quantities in the following line are real numbers):

$$J_L = \frac{\hbar k}{m} \left(1 - \left| \frac{B}{A} \right|^2 \right) |A|^2 = \frac{\hbar k}{m} \left(1 - \left(\frac{k - \bar{k}}{k + \bar{k}} \right)^2 \right) |A|^2 = \frac{\hbar k}{m} \left(\frac{4k\bar{k}}{(k + \bar{k})^2} \right) |A|^2 = \frac{\hbar \bar{k}}{m} \left(\frac{2k}{k + \bar{k}} \right)^2 |A|^2 = \frac{\hbar \bar{k}}{m} |C|^2 = J_R.$$

(And in fact, because this conservation law comes from Schrodinger's equation, it makes sense that the relations between A , B , and C are also encoded in that equation.) But because the solution $\psi(x)$ is made up of two different oscillating components, we can also write $J_L = J_A - J_B$, where $J_A = \frac{\hbar k}{m} |A|^2$ and $J_B = \frac{\hbar k}{m} |B|^2$ are the probability currents brought by the incoming and reflected waves alone. (We'll thus also write $J_R = J_C$.) This suggests that we should define **reflection and transmission coefficients** in terms of this current:

$$R = \frac{J_B}{J_A} = \left| \frac{B}{A} \right|^2, \quad T = \frac{J_C}{J_A} = \frac{\bar{k}}{k} \left| \frac{C}{A} \right|^2$$

Essentially, a reflection coefficient of 0.1 would indicate that if we put particles into this potential from the left, then 10 percent of them would be reflected. (We don't actually have particles yet, but this is the intuition!) And importantly, T is not just $\left| \frac{C}{A} \right|^2$, as we might be tempted to write – **the coefficients originate from probabilities, not amplitudes**. With these definitions, we can notice that (because $J_A - J_B = J_C$)

$$R + T = \frac{J_B}{J_A} + \frac{J_C}{J_A} = 1,$$

as we should expect with reflection and transmission coefficients in general. And when we have a wavepacket instead of a pure energy eigenstate, there will be some uncertainty in position and momentum, but the reflection and transmission probabilities will be basically given by R and T if the packet is localized near some particular energy.

Example 117

We'll now continue our study of the step potential, looking at the $E < V_0$ case.

The idea is to trust the principle of analytic continuation here (luckily, in this case it's not quite as complicated as the mathematical words might suggest), which basically means that we can write down the same solution for $x < 0$ as before (since the energy E is still positive), with $k^2 = \frac{2mE}{\hbar^2}$. And for $x > 0$, we just replace the $e^{i\bar{k}x}$ with an $e^{-\kappa x}$ (the form of the solution we know to expect). This is achieved by replacing \bar{k} with $i\kappa$ everywhere, which means that

$\kappa^2 = \frac{2m(V_0 - E)}{\hbar^2}$ (we just pick up a negative sign). We could have also replaced \bar{k} with $-i\kappa$, but the reason for our choice here is that we now have

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0, \\ Ce^{-\kappa x} & x \geq 0, \end{cases}$$

and ψ decays exponentially to zero as $x \rightarrow \infty$, as it should. And by doing this, we save the time of having to compute $\frac{B}{A}$ and $\frac{C}{A}$ by matching continuity of ψ and ψ' again; instead, we can just replace \bar{k} with $i\kappa$. We thus find that

$$\frac{B}{A} = \frac{k - i\kappa}{k + i\kappa} = \frac{-i(\kappa + ik)}{i(\kappa - ik)} = -\frac{\kappa + ik}{\kappa - ik},$$

which is a ratio of two complex numbers of the same magnitude. In other words (imagining a right triangle formed by the points 0, k , and $k + i\kappa$ in the complex plane), we have $\frac{B}{A} = -e^{2i\delta(E)}$, where

$$\delta(E) = \tan^{-1} \frac{\kappa}{k} = \tan^{-1} \sqrt{\frac{E}{V_0 - E}}$$

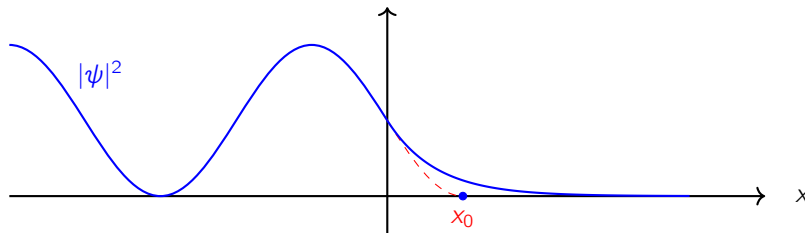
is a phase shift that depends on the energy of the eigenstate. But $\frac{C}{A}$ no longer plays the same role that it originally did – because we have a purely real solution for $x > 0$ this time, the probability current is zero (because ψ decays, the particle cannot have a positive rates of moving to the right). Instead, we have $J_C = 0$ and $J_A = J_B$ (consistent with $|A|^2 = |B|^2$ as discussed above). With this, we can rewrite the solution as

$$\psi(x) = \begin{cases} Ae^{ikx} - Ae^{2i\delta(E)}e^{-ikx} & x < 0, \\ Ce^{-\kappa x} & x > 0 \end{cases},$$

and we can rewrite the solution for $x < 0$ as

$$Ae^{i\delta(E)} \left(e^{i(kx - \delta(E))} - e^{-i(kx - \delta(E))} \right) = \boxed{2iAe^{i\delta(E)} \sin(kx - \delta(E))},$$

so that $|\psi(x)|^2 = 4|A|^2 \sin^2(kx - \delta(E))$. If we let $x_0 = \frac{\delta(E)}{k}$ be the first positive x -coordinate where this probability density is zero, then we have the following sketch for $|\psi|^2$:



Since $\delta(E)$ ranges from 0 to $\frac{\pi}{2}$ as E ranges from 0 to V_0 (and in fact the derivative $\frac{d\delta}{dE} = \frac{1}{2} \sqrt{\frac{1}{E(V_0 - E)}}$ is large near $E = 0$ and $E = V_0$), we see that near $E = 0$ the probability density is close to zero at $x = 0$, but near $E = V_0$ the probability density is near its maximum.

Example 118

We can now connect this solution form to a physical problem by considering **wavepackets** – this is very similar to past discussions with the principle of stationary phase.

We'll start by considering $E > V_0$ (so that we do have a transmitted wave), and we'll set $A = 1$ first:

$$\psi(x) = \begin{cases} e^{ikx} + \left(\frac{k-\bar{k}}{k+\bar{k}}\right) e^{-ikx} & x < 0, \\ \frac{2k}{k+\bar{k}} e^{i\bar{k}x} & x > 0. \end{cases}$$

We'll now superimpose waves of this form. First, we need to add the time-dependent factor $e^{-iEt/\hbar}$ to our whole solution, then we need to pick the coefficient $f(k)$ with which this solution appears, and finally we superimpose all such solutions by integrating over k :

$$\Psi(x, t) = \begin{cases} \int_0^\infty f(k) \left(e^{ikx} + \left(\frac{k-\bar{k}}{k+\bar{k}}\right) e^{-ikx} \right) e^{-iEt/\hbar} dk & x < 0, \\ \int_0^\infty f(k) \frac{2k}{k+\bar{k}} e^{i\bar{k}x} e^{-iEt/\hbar} dk & x > 0. \end{cases}$$

The key point here is that we can choose the bounds of integration (since we're creating our own superposition of valid solutions to the Schrodinger equation), and we should **not** integrate from $-\infty$ to ∞ because only the $k > 0$ solutions correspond to an incoming packet moving to the right. Furthermore, to ensure that we have a localized packet, $f(k)$ should be sharply peaked around some $k = k_0$. (In the past, the only way to compute this kind of integral numerically was with a supercomputer, but we can quickly do it on a laptop now.) We'll split up the integral a bit by letting the **incident wave**, only defined for $x < 0$, be

$$\Psi_{\text{inc}}(x, t) = \int_0^\infty f(k) e^{ikx} e^{-iEt/\hbar} dk,$$

letting the **reflected wave**, also only defined for $x < 0$, be

$$\Psi_{\text{ref}}(x, t) = \int_0^\infty f(k) \left(\frac{k-\bar{k}}{k+\bar{k}}\right) e^{-ikx} e^{-iEt/\hbar} dk,$$

and letting the **transmitted wave**, only defined for $x > 0$, be

$$\Psi_{\text{trans}}(x, t) = \int_0^\infty f(k) \frac{2k}{k+\bar{k}} e^{i\bar{k}x} e^{-iEt/\hbar} dk.$$

In particular, the total wavefunction is $\Psi(x, t) = \begin{cases} \Psi_{\text{inc}}(x, t) + \Psi_{\text{ref}}(x, t) & x < 0, \\ \Psi_{\text{trans}}(x, t) & x > 0, \end{cases}$, and now we need to go a bit

further by making the stationary phase approximation to understand how the wave packet is actually moving. Because $f(k)$ appears in every integral in $\Psi(x, t)$ and is very sharply peaked at $k = k_0$, we can say that the wavefunction only has contributions from $k \approx k_0$ and get a pretty accurate estimate. We'll take $f(k)$ to be real, so that there's no associated phase to it, and recall that the stationary phase approximation requires that the k -derivative of the phase is zero.

- For the **incident wave**, this means that

$$\frac{d}{dk} \left(kx - \frac{Et}{\hbar} \right)_{k=k_0} = 0 \implies x - \frac{\hbar k_0}{m} t = 0 \implies x = \frac{\hbar k_0}{m} t,$$

since $E = \frac{\hbar^2 k^2}{2m}$, and this means that **the incident wave is propagating to the right** at speed $\frac{\hbar k_0}{m}$ for $t < 0$ (this is consistent because Ψ_{inc} is only defined for negative x anyway), and it "hits the barrier" at $x = 0$ at time zero – after that, Ψ_{inc} will be approximately zero, since we only look at negative x .

- For the **reflected wave**, our condition is similarly that

$$\frac{d}{dk} \left(-kx - \frac{Et}{\hbar} \right)_{k=k_0} = 0 \implies x = -\frac{\hbar k_0}{m} t.$$

This also makes sense in that the **reflected wave propagates to the left** at a speed $\frac{\hbar k_0}{m}$ for $t > 0$ and only significantly contributes to the wavefunction after the incident wave hits the barrier.

- Finally, for the **transmitted wave**, the calculation is more complicated because we have \bar{k} instead of k , and taking a derivative of \bar{k} with respect to k is more interesting. It turns out that we will have $x = \frac{\hbar \bar{k}}{m} t$ (and because Ψ_{trans} only exists for $x > 0$, this is only significant for $t > 0$), and this means that the **transmitted wave propagates to the right**, but at a different speed.

We will now consider wavepackets for $E < V_0$ – a similar strategy for superposition gives us the incident wave (for $x < 0$)

$$\Psi_{\text{inc}}(x, t) = \int_0^\infty f(k) e^{ikx} e^{-iEt/\hbar} dk$$

and the corresponding reflected wave (also for $x < 0$, this time referring to our discussion of phase $\delta(E)$ from above)

$$\Psi_{\text{ref}}(x, t) = - \int_0^\infty f(k) e^{-ikx} e^{2i\delta(E)} e^{-iEt/\hbar} dk.$$

The transmitted wave is much less interesting in this case, because there really isn't a transmitted wave at all. Instead, what's happening physically here is that we send in a wavepacket, look at the reflected shape, and use that to deduce the type of potential that the particle encountered. The stationary phase approximation again gives us $x = \frac{\hbar k_0}{m} t$ for the incoming wave, but this time the reflected wave is more complicated:

$$\frac{d}{dk} \left(-kx + 2\delta(E) - \frac{Et}{\hbar} \right)_{k=k_0} = 0 \implies x = -\frac{\hbar k_0}{m} (t - 2\hbar\delta'(E)).$$

Since the reflected wave is only defined on $x < 0$, we see that we get a significant contribution when $t > 2\hbar\delta'(E)$, or approximately when t is positive, like before. But because of this additional $2\hbar\delta'(E)$ term, the wave does not bounce perfectly off the barrier at $x = 0$; there is a **time delay** of $2\hbar\delta'(E)$ (which is large for E near 0 or V_0 , as previously discussed), and this type of expression is what is used in scattering theory to determine the type of potential we're scattering off.

To finish this lecture, we'll think a bit about the forbidden region (where $x > 0$ and $E < V_0$) and what the decaying exponential wavefunction means. In particular, we may ask what a particle looks like if we find it to have energy $E < V_0$, meaning that it has negative kinetic energy. It would be contradictory to say both that the particle is in the forbidden region and that it has energy less than V_0 , and quantum mechanics evades this problem (this is not a completely precise argument, but it's enough to get the intuition) by arguing about **uncertainty**. Specifically, because the wavefunction decays as $e^{-\kappa x}$, the length scale at which we are likely to find the particle is on the order of $\frac{1}{\kappa}$ (recalling that $\kappa^2 = \frac{2m(V_0 - E)}{\hbar^2}$). But to say that the particle is in the forbidden region, we need to measure the particle with uncertainty $\Delta x < \frac{1}{\kappa}$, and thus the particle has an uncertainty in momentum $p > \frac{\hbar}{\Delta x} = \hbar\kappa$. This uncertainty then gives us a "uncertainty" kinetic energy of

$$KE = \frac{p^2}{2m} = \frac{\hbar^2 \kappa^2}{2m} = V_0 - E,$$

and thus the "negative kinetic energy" is compensated for by the uncertainty in momentum – the total energy of the particle is now $E + (V_0 - E) = V_0$, and no contradiction arises – we'll just find a normal particle in the region $x > 0$.

Lecture 17: Ramsauer-Townsend and General Scattering

We'll continue our discussion of scattering states today – last lecture, we analyzed the behavior of reflection and transmission under a step potential, and today we'll explore a different effect called **resonance transmission** (and how it leads to the Ramsauer-Townsend effect) before turning to more general resonance problems. First, we will do a toy problem with the finite square well:

Example 119

Consider the one-dimensional system given by the potential

$$V(x) = \begin{cases} -V_0 & -a < x < a \\ 0 & \text{otherwise,} \end{cases}$$

and suppose we send an incoming wave into the potential from the left (meaning that we are looking for **scattering states** of $E > 0$).

We are interested in understanding reflection and transmission coefficients, but we know from last lecture's discussion that energy eigenstates tell us most of the story – if a wavepacket is localized around some energy, then it'll behave like an energy eigenstate of that energy. At both $x = -a$ and $x = a$, the discontinuity in the potential means there may be reflection and transmission, and physically we can imagine that the particle might "bounce back and forth" repeatedly between those two points.

Remark 120. *In quantum mechanics, reflection and transmission can occur whether the potential goes up or down – this is different from the classical case in which we can only reflect off of a higher barrier.*

Even though many reflections may occur, we will still have $\psi(x) = Ae^{ikx} + Be^{-ikx}$ in the region $x < -a$, and similarly we will have $\psi(x) = Ce^{ik_2x} + De^{-ik_2x}$ (different wavenumber because we have a different kinetic energy) in the region $-a < x < a$. In particular (by the same logic as usual), we have $k^2 = \frac{2mE}{\hbar^2}$ and $k_2^2 = \frac{2m(E+V_0)}{\hbar^2}$. Finally, we will only have $\psi(x) = Fe^{ikx}$ in the region (no wave moving to the left) because there is nothing to bounce off of past $x = a$. Putting everything together,

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx}, & x < -a \\ Ce^{ik_2x} + De^{-ik_2x}, & -a < x < a \\ Fe^{ikx} & x > a. \end{cases}$$

We'll reason about these coefficients by thinking about **probability current**, since we've already seen that this is a good way to know how to define reflection and transmission coefficients. With the step potential, we had an extra factor beyond the $|\frac{C}{A}|^2$ because the two sides of the barrier were at different energies, but in this case the two sides of the square well are at the same energy. Thus, it's reasonable to believe that we just have

$$R = \left| \frac{B}{A} \right|^2, \quad T = \left| \frac{F}{A} \right|^2$$

in this case, and this will make sense if it turns out that $R + T = 1$. Indeed, following the current conservation calculations from last time, we know that $J_L \sim |A|^2 - |B|^2$ (the current to the left of $x = -a$) and $J_R \sim |F|^2$ (the current to the right of $x = a$), with the same proportionality constant, so $|A|^2 - |B|^2 = |F|^2$ and we do have $R + T = 1$.

But to actually calculate those ratios, we do need to do some work – there are five variables and four boundary conditions (two at each discontinuity), which makes sense because there's one free variable of overall normalization.

We'll skip those calculations here – it turns out that

$$\frac{1}{T} = 1 + \frac{1}{4} \frac{V_0^2}{E(E + V_0)} \sin^2(2k_2a)$$

(notice that the second term on the right-hand side is nonnegative, so T is indeed between 0 and 1). Looking at some relevant limits, if $\sin^2(2k_2a) \rightarrow 0$ or $E \rightarrow \infty$, then we actually have $T \rightarrow 1$, giving us complete transmission (we'll discuss this more soon), and if $E \rightarrow 0$, we have $T \rightarrow 0$, giving us no transmission. To understand this more, we can rewrite this expression in unit-free language: notice that

$$2k_2a = 2\sqrt{\frac{2ma^2(E + V_0)}{\hbar^2}} = 2\sqrt{\frac{2ma^2V_0(1 + \frac{E}{V_0})}{\hbar^2}} = 2\sqrt{z_0^2(1 + e)} = 2z_0\sqrt{1 + e},$$

where we define the unit-free energy $e = \frac{E}{V_0}$ (relative to the depth of the potential) and $z_0^2 = \frac{2ma^2V_0}{\hbar^2}$ should look familiar from our past discussions of the finite square well. Similarly simplifying the prefactor in terms of e gives us

$$\boxed{\frac{1}{T} = 1 + \frac{1}{4e(1 + e)} \sin^2(2z_0\sqrt{1 + e})}$$

As we mentioned above, we are now interested in the energies E for which $T = 1$, which means that $2z_0\sqrt{1 + e} = n\pi$ for some integer n . (Furthermore, because $\sqrt{1 + e} \geq 1$, we must have $n \geq \frac{2z_0}{\pi}$.) Rearranging, we find that

$$4z_0^2(1 + e_n) = n^2\pi^2 \implies e_n = -1 + \frac{n^2\pi^2}{4z_0^2} \implies E = -V_0 + \frac{n^2\pi^2V_0}{4z_0^2} = -V_0 + \frac{n^2\pi^2V_0}{2ma^2V_0/\hbar^2} = \boxed{-V_0 + \frac{n^2\pi^2\hbar^2}{2m(2a)^2}}$$

In this form, the answer can actually make some intuitive sense: we have **resonant transmission** (meaning $T = 1$) if the distance between the energy E and the bottom of well $-V_0$ is $\frac{n^2\pi^2\hbar^2}{2m(2a)^2}$, which is the energy level of an **infinite** (rather than finite) square well of width $2a$. And this is really because from the point of view of the wavefunction, the condition that $k_2(2a) = n\pi$ (for resonant transmission) is the same as $\frac{(2a)}{\lambda} = \frac{n}{2}$. In other words, the de Broglie wavelength of the particle inside the well fits a half-integer number of times inside the well of length $2a$, and the energy eigenstate passes completely through the well in this case.

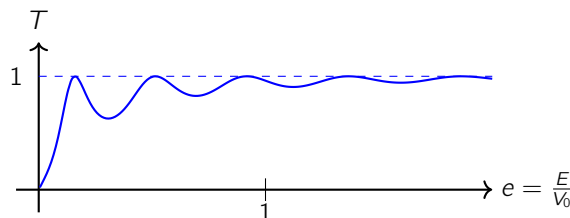
Example 121

For a numerical example, suppose we have a square well where $z_0 = \frac{13\pi}{4}$, so that we only get valid energies E when $n \geq \frac{2z_0}{\pi} = \frac{13}{2}$.

(In other words, we need to start from the seventh lowest energy of the infinite square well to get a positive E .) We can then plug in numerically to find that

$$e_7 = \frac{E_7}{V_0} \approx 0.15976, e_8 = \frac{E_8}{V_0} \approx 0.51479, e_9 = \frac{E_9}{V_0} \approx 0.91716.$$

More generally, here is a plot of the transmission probability as a function of $e = \frac{E}{V_0}$:



Example 122

We're now ready to talk about a famous experiment performed by Ramsauer and Townsend (two physicists) in 1921, **elastic scattering of electrons off of rare gas atoms**.

Here, "elastic scattering" means that no particles are created or destroyed, and the gas atoms have completely full outer shells (so that they are inert noble gases and have high ionization energies). That means that we can essentially visualize the gas atoms as a spherical cloud around a central nucleus, and from the point of view of an electron (by Gauss's law) there will be no electric field until we enter the cloud. At that point, the electric field will point inward, so the electron will curve towards the nucleus and eventually exit the cloud at a different angle. So this is kind of like a finite **spherical well**, analogous to the finite square well we've been discussing above!

To turn this into a situation where reflection and transmission coefficients make sense, we can say that particles are reflected if they scatter significantly and are transmitted if they pass through. (More mathematically, we could talk about the scattering cross-section.) But what experiments found was that the reflection coefficient R (as a function of e) also exhibited this "bouncy" behavior as in the plot above, starting off very high but reaching a local minimum around 1 eV (which corresponds to the electron moving at around 600 kilometers per second). And this sensitivity of the reflection coefficient to the energy of the particle comes from a very similar reasoning of resonance within the well! But the explanation didn't come until years later when quantum mechanics was more fully developed, and if we want the exact numbers we'll have to do a three-dimensional version of the calculation above.

In the rest of this lecture (and the next few as well), we'll now expand our discussion to more general one-dimensional scattering.

Example 123

Suppose we have a one-dimensional system where there is an infinite barrier left of $x = 0$ and a finite R above which the potential is zero (called the **range** of the potential):

$$V(x) = \begin{cases} 0 & x > R, \\ V(x) & 0 < x < R, \\ \infty & x < 0. \end{cases}$$

The scattering is performed by having an observer "throw" incoming waves in from $x = +\infty$, which reflect off of the barrier. We then wish to measure the outgoing wave to deduce information about the potential, and this is indeed what is done in particle colliders in modern physics when multiple particles interact with each other.

Remark 124. *The infinite barrier left of $x = 0$ makes sense if we think about x as taking the place of the radial coordinate r in three dimensions – it's never possible to be a negative distance away from the origin. And in a future quantum physics course, we might study scattering in three dimensions, and this will be a useful tool in that discussion.*

We'll begin with the simplest case where $V(x) = 0$ for $0 < x < R$, and thus we are just scattering off of an infinite wall with **no additional potential**. Incident and outgoing waves will then look like e^{-ikx} and e^{ikx} respectively (both are energy eigenstates and thus valid solutions), and we can combine these together into a solution to the Schrodinger equation of the form

$$\phi(x) \sim e^{ikx} - e^{-ikx}$$

so that the wavefunction is zero at $x = 0$. Remembering that $\sin x = \frac{e^{ix} - e^{-ix}}{2i}$, we thus get the solution $\phi(x) = \sin(kx)$ for $x > 0$, but we can still think of this as being a combination of an incoming ($-\frac{e^{-ikx}}{2i}$) and outgoing ($\frac{e^{ikx}}{2i}$) plane wave.

This gives us an inspiration for what to write in the more general case with a nonzero potential: we'll have an incoming wave $-\frac{e^{-ikx}}{2i}$ just like before, but that is only valid for $x > R$ (because plane waves are not energy eigenstates when the potential is nonzero). The outgoing wave is then going to be of the form $c\frac{1}{2i}e^{ikx}$ for some constant c (that's the only other energy eigenstate at energy E besides e^{-ikx}), but remembering our discussion about probability current, we must actually have $|c| = 1$ by conservation of probability (there is no transmission to $x < 0$, and in a stationary state we cannot have probability accumulating or depleting inside the potential).

In summary, **the potential can only influence the outgoing plane wave by a phase**, and we'll write the outgoing wave as $\frac{1}{2i}e^{ikx}e^{2i\delta}$ for some phase δ . (And remembering that δ depends on the energy E of the plane waves we're sending in, we see that we can get δ as a function of E or k , which can give us substantial information about $V(x)$.) The phase is only defined up to a multiple of 2π , but for reasons we'll see next lecture, it turns out to be convenient to **fix the phase δ at $k = 0$ and then make the phase continuous as a function of k** (so if it keeps going clockwise, we keep increasing it even past 2π). The total solution to the Schrodinger equation, incoming plus reflected, is thus

$$\psi(x) = \frac{1}{2i} (e^{ikx+2i\delta} - e^{-ikx}) = \frac{e^{i\delta}}{2i} (e^{i(kx+\delta)} - e^{-i(kx+\delta)}) = \boxed{e^{i\delta} \sin(kx + \delta)}$$

for $x > R$. (And if $\delta = 0$, we're back to the original wavefunction for the "no potential" case.)

Comparing the probability density $|\phi(x)|^2 = \sin^2(kx)$ (no potential) with $|\psi(x)|^2 = \sin^2(kx + \delta)$ (with potential), we see that the same features of the wavefunctions (maximums, nodes, and so on) occur in both cases, but shifted by a constant distance $-\frac{\delta}{k}$. (Specifically, $kx = a_0$ occurs at $x = \frac{a_0}{k}$, but $kx + \delta = a_0$ occurs at $x = \frac{a_0}{k} - \frac{\delta}{k}$.) So when $\delta > 0$, the wavefunction is pulled into the potential (in other words, the potential is attractive), and when $\delta < 0$, the wavefunction is pushed outward (the potential is repulsive). And in preparation for next lecture, we'll make the following definition:

Definition 125

The **scattered wave** $\psi_s(x)$ is the extra component of the wavefunction added from the no-additional-potential case, defined via

$$\psi(x) = \phi(x) + \psi_s(x).$$

Remembering that ψ and ϕ were defined to have the same incoming wave $-\frac{e^{-ikx}}{2i}$, we see that ψ_s represents how much more of an outgoing wave we get with the potential between 0 and R , and it must be an outgoing wave itself. And because we have the explicit expressions for the two waves, we see that

$$\psi_s(x) = \psi(x) - \phi(x) = \frac{1}{2i} (e^{ikx+2i\delta} - e^{-ikx}) - \frac{1}{2i} (e^{ikx} - e^{-ikx}) = \frac{e^{ikx}}{2i} (e^{2i\delta} - 1) = \boxed{e^{ikx} e^{i\delta} \sin \delta}.$$

In other words, this additional scattered wave is zero when $\delta = 0$ (representing that no change occurred), and the amplitude of this additional outgoing wave is $e^{i\delta} \sin \delta$. We'll make use of this next time!

Lecture 18: Phase Shift and Levinson's Theorem

Last lecture, we introduced the general scattering problem for a finite-range potential of length R , in which we work with a potential $V(x)$ which is infinite for $x < 0$ and zero for $x > R$. Specifically, we look at energy eigenstates of energy $E = \frac{\hbar^2 k^2}{2m}$, and we can compare the solution $\phi(x) = \sin kx$ (a combination of an incoming and outgoing wave $-\frac{e^{-ikx}}{2i} + \frac{e^{ikx}}{2i}$) when the potential is zero on $(0, R)$ with the solution

$$\psi(x) = e^{i\delta} \sin(kx + \delta) = -\frac{e^{-ikx}}{2i} + \frac{e^{2i\delta} e^{ikx}}{2i}$$

(only valid on $x > R$) when we do have a nonzero potential. As mentioned at the end of last lecture, we often write $\psi(x) = \phi(x) + \psi_s(x)$, where the scattered wave turns out to be the outgoing wave $\psi_s(x) = e^{i\delta} \sin \delta e^{ikx}$ for $x > R$. Here, $A_s = e^{i\delta} \sin \delta$ is called the **scattering amplitude**, and we are often interested in $|A_s|^2 = \sin^2 \delta$ to quantify the effect of the nonzero potential.

Today, we'll connect this to the concept of **time delay** by calculating what happens when we send in wavepackets into this potential. (Recall that we've previously discussed this in the context of the step potential.) If we have an incident wave of the form

$$\Psi_{\text{inc}}(x, t) = \int_0^\infty f(k) e^{-ikx} e^{-iE(k)t/\hbar} dk$$

in the region $x > R$ (here we put back the time dependence to get the time-dependent wavefunction), then we know the reflected wave that corresponds to it will be

$$\Psi_{\text{ref}}(x, t) = - \int_0^\infty f(k) e^{ikx} e^{2i\delta(E)} e^{-iE(k)t/\hbar} dk$$

in the region $x > R$ (negative sign and $e^{2i\delta}$ factors coming from the expression for the reflected wave). As usual, $f(k)$ will be a real function that peaks sharply at some $k = k_0$. And now we can keep track of how the peak of the wavepacket moves by doing the usual stationary phase approximation at $k = k_0$ – we'll skip the calculations because we've done them a few times already. The incident wave turns out to satisfy $x = -\frac{\hbar k_0}{m} t = -v_g t$ for a constant group velocity v_g (and this is only valid for $t < 0$), while the reflected wave satisfies $x = v_g(t - 2\hbar\delta'(E))$. So the reflected wave moves at the same group velocity as the incident wave, but it only starts to appear after a **delay** (which can be positive or negative) of

$$\Delta t = 2\hbar\delta'(E) = 2\hbar \frac{d\delta}{dk} \frac{dk}{dE} = \frac{2}{\frac{1}{\hbar} \frac{dE}{dk} \Big|_{k=k_0}} \frac{d\delta}{dk} \Big|_{k=k_0} = \frac{2}{v_g} \frac{d\delta}{dk} \Big|_{k=k_0}$$

(we have total rather than partial derivatives, so there's nothing to worry about with these manipulations). This equation can be further manipulated to

$$\frac{1}{R} \frac{d\delta}{dk} = \frac{\Delta t}{2R/v_g}.$$

This is now a unitless relation, and the right-hand side compares the time delay Δt to the time it takes to traverse the finite-range potential and back (length $2R$) at the group velocity v_g ! So this ratio of the delay to the **free transit time** gives us a sense of whether the potential has caused a significant delay in how the wavepacket travels.

We'll now do an example where we can calculate everything explicitly (though the formulas may still be rather messy and are only insightful if we plot with a computer):

Example 126

Suppose we have a potential well of length a , meaning that our potential is of the form (for some $V_0 > 0$)

$$V(x) = \begin{cases} \infty & x < 0, \\ -V_0 & 0 < x < a, \\ 0 & \text{otherwise,} \end{cases}$$

and we wish to explicitly calculate energy eigenstates of energy $E > 0$.

Since this falls under the general setup we've been using, we know already that $\psi(x) = e^{i\delta} \sin(kx + \delta)$ for $x > a$ (this is the specific combination of e^{ikx} and e^{-ikx} that is necessary), where $k^2 = \frac{2mE}{\hbar^2}$ as usual. And for $0 < x < a$, we must have a combination of $e^{ik'x}$ and $e^{-ik'x}$, where $k'^2 = \frac{2m(E+V_0)}{\hbar^2}$, but it is convenient to use trig functions instead

– we can only have something proportional to $\sin(k'x)$ because the wavefunction must vanish at 0. This gives us the ansatz (not putting an additional normalization in the $x > a$ case just to remove a variable)

$$\psi(x) = \begin{cases} e^{i\delta} \sin(kx + \delta) & x > a, \\ A \sin(k'x) & x < a, \end{cases}$$

with the additional boundary conditions that ψ and ψ' must be continuous at $x = a$, meaning that

$$A \sin(k'a) = e^{i\delta} \sin(ka + \delta), \quad Ak' \cos(k'a) = k e^{i\delta} \cos(ka + \delta).$$

Much like with the finite square well, we can divide the two equations to get

$$k' \cot(k'a) = k \cot(ka + \delta) \implies \cot(ka + \delta) = \frac{k'}{k} \cot(k'a).$$

We can now isolate δ by taking \cot^{-1} on both sides, but there's a bit of trigonometric manipulation we can do now: specifically, we can use the fact that $\cot(A + B) = \frac{\cot A \cot B - 1}{\cot A + \cot B}$ and then solve for $\cot \delta$, which yields

$$\cot \delta = \frac{\tan(ka) + \frac{k'}{k} \cot(k'a)}{1 - \frac{k'}{k} \cot(k'a) \tan(ka)}.$$

Given any value of the energy E , we can then calculate k' and k and find the phase shift by plugging in those values. But if we want to plot this on a computer, the right variables are the unitless ones such as ka and $k'a$: define

$$u^2 = (ka)^2 = \frac{2mEa^2}{\hbar^2},$$

so that

$$(k'a)^2 = \frac{2mEa^2}{\hbar^2} + \frac{2mV_0a^2}{\hbar^2} = u^2 + z_0^2$$

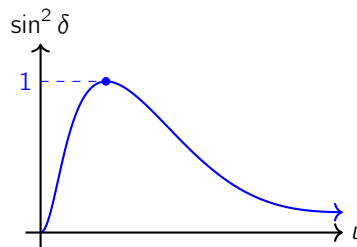
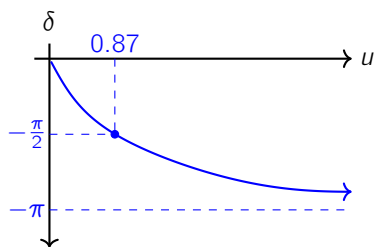
with the standard unit-free length scale z_0 for the finite square well! So now taking the reciprocal of both sides of the boxed equation, and using the fact that $\frac{k'a}{ka} = \sqrt{1 + \frac{z_0^2}{u^2}}$, we have

$$\tan \delta = \frac{1 - \frac{(k'a)}{ka} \cot(k'a) \tan(ka)}{\tan(ka) + \frac{k'a}{ka} \cot(k'a)} = \frac{1 - \sqrt{1 + \frac{z_0^2}{u^2}} \cot \sqrt{z_0^2 + u^2} \tan u}{\tan u + \sqrt{1 + \frac{z_0^2}{u^2}} \cot \sqrt{z_0^2 + u^2}},$$

and now z_0 is a property of the potential well we're given – for any well of depth V_0 and width a , we can plug in the constant z_0 and plot $\tan \delta$ as a function of u . And notice that as $u \rightarrow 0$, the numerator approaches a constant (because the $\sqrt{1 + \frac{z_0^2}{u^2}}$ diverging and $\tan u$ going to zero balance each other out), while the denominator goes to infinity because of the second term. So $\tan \delta \rightarrow 0$ as $u \rightarrow 0$, and **we can pick the phase shift to be $\delta = 0$ for $u = 0$** (rather than 2π , for example).

We can now study the behavior of δ versus $u = ka$ for various values of z_0 :

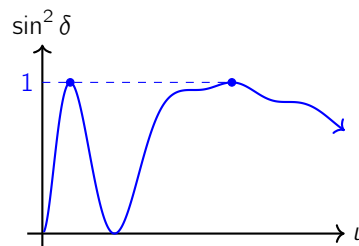
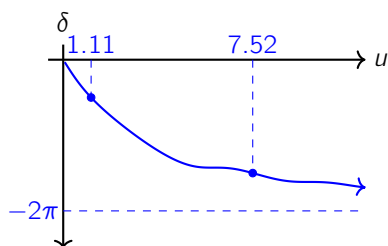
- When $z_0^2 = 3.4$ (corresponding to $z_0 \approx 0.59\pi$), $\delta(u)$ starts off at 0, becomes more negative, and then stabilizes at $-\pi$ for large u . The scattering amplitude is strongest when $\delta = -\frac{\pi}{2}$, so $\sin^2 \delta$ peaks once. Finally, the unit-free delay (the derivative $\frac{d\delta}{du}$) starts around -4 and asymptotically goes to zero. The plots of δ and $\sin^2 \delta$ are shown below:



In particular, notice that a **negative time delay** corresponds to the packet coming back earlier than ordinarily expected. But this makes sense, because the kinetic energy of the packet increases when the potential is lower and thus the group velocity is larger.

As a sidenote, if we plot the amplitude A as a function of u , we get a graph similar to that in Example 121.

- The behavior remains very similar as we increase z_0 , until a sudden change happens. In particular, by the time we are at $z_0 = 5$, the graphs look as shown below (with the two circles indicating the points at which δ crosses $-\frac{\pi}{2}$ and $-\frac{3\pi}{2}$):



Exploring the limiting behavior of δ for different values of z_0 , we see that it either goes back to 0 (for small z_0), or it approaches one of $-\pi$, -2π , -3π , and so on. And it turns out that the fundamental relation relates **the overall excursion in the phase δ to the number of bound states of the potential!** We can check as an exercise that for this “half-square well,” this potential has all of the odd bound states of the full finite square well, and we found (see calculations in Example 91) that we determine how many of these solutions we have by seeing if z_0 is larger than specified multiples of $\frac{\pi}{2}$.

It turns out these numbers will indeed increase at the same time, and this leads us to **Levinson’s theorem**. This is the most subtle derivation we’ll do in this class, and we’ll need to use the following fact:

Fact 127

As we vary a potential, the energy eigenstates will vary, but they do not appear or disappear.

This may seem confusing given our discussion above, but when we think about the states of (for example) a finite square well, we should remember that **there are an infinite number of scattering states** above the finitely many bound states! So if we decrease the depth of a finite square well, eventually the highest-energy bound state will change into a scattering state. And if we increase the depth, eventually the scattering states will “lend” the bound states an extra state. This may seem like an argument that doesn’t make much sense because we have uncountably infinitely many states, but one way to make this rigorous is to imagine putting this whole system in a very large box of length L , making even the positive-energy states discrete. Then as we change the depth of our well, we’ll indeed see the states of positive energy drop down and change into states of negative energy, and still nothing is created or destroyed.

Theorem 128 (Levinson's theorem)

Suppose we are in the finite-range potential setting in Example 123. Then the number of bound states N of the potential is predicted by the behavior of scattering via

$$N = \frac{1}{\pi} (\delta(0) - \delta(\infty)).$$

Proof. Motivated by the discussion above, in order to avoid a continuum of states, we will also place an infinitely high potential barrier for $x > L$, where $L \gg R$. (This is sometimes called a **regulator**.) Then our states will be quantized, and for large L , they will be close to each other and look a lot like scattering states (but still be bound states in reality). And we'll take the limit as $L \rightarrow \infty$ – if the answer doesn't depend on L , then we can claim the answer holds in the limit as well.

If we think about the case with no potential $V(x)$, then all energy eigenstates have positive energy and are of the form $\phi(x) = \sin(kx)$, where $\phi(L) = 0$ (boundary conditions for an infinite square well). Thus, we require $kL = n\pi$ for some positive integer n , and now indeed k can only take on integer multiples of $\frac{\pi}{L}$ (meaning that the energy states are discrete). Within a differential dk , we then have $\frac{\pi}{L} dn$ positive energy states in that range.

On the other hand, in the case where we do have a potential, we can't solve the Schrodinger equation in general, but we do know that we have the universal solution $\psi(x) + e^{i\delta} \sin(kx + \delta)$ in the region $R < x < L$, and again we must demand $\psi(L) = 0$. So this time we require $kL + \delta(L) = n'\pi$ for some integer n' , meaning that for any interval dk , the number of positive energy states is given by

$$Ldk + \frac{d\delta}{dk} dk = \pi dn' \implies dn' = \frac{L}{\pi} dk + \frac{1}{\pi} \frac{d\delta}{dk} dk.$$

If we then look over the entire range of k -values (in the positive real axis), we can count the **difference in the number of positive-energy states**. In particular, if we imagine doing a slow deformation from $V = 0$ to $V = V(x)$, the states will also slowly vary (using the logic of Fact 127), and we can count how many energy states are gained or lost in that interval:

$$\text{positive-energy states lost in } dk \text{ when potential is turned on} = dn - dn' = -\frac{1}{\pi} \frac{d\delta}{dk} dk,$$

and thus the total number of energy states lost overall is the integral

$$\text{positive-energy states lost} = \int_0^\infty -\frac{1}{\pi} \frac{d\delta}{dk} dk = \frac{1}{\pi} (\delta(0) - \delta(\infty)).$$

because the integrand is just a total derivative. But (again by Fact 127) those states cannot disappear – they must have become bound states. Since we have zero bound states at $V = 0$, the number of bound states for the potential $V(x)$ must be the boxed quantity above. \square

In particular, this argument gets around the fact that we have infinitely many scattering states in both cases – by counting the **differences** in number of states in infinitesimal regions, we are able to reason about the count of the finitely many bound states.

Lecture 19: Resonance and Time Delay

Today's lecture will explore more on **resonances** in scattering theory – we've seen some of this in the **resonant transmission** of the Ramsauer-Townsend effect, in which particles move past a potential without any reflection for

some particular energies E .

We'll start with the same setting as last lecture, with a finite-range potential within $0 < x < R$ and an infinite barrier for $x < 0$. Our first question will concern the **time delay** $2\hbar \frac{d\delta(E)}{dE}$, which we know can be positive or negative – specifically, we want to ask if the time delay can be **arbitrarily negative** (meaning that the packet comes back much earlier than if we had no potential). The answer is **no** – essentially, it wouldn't make sense if the particle came back earlier than if there was a hard (infinite) wall at $x = R$, because there's nowhere for the particle to be reflected before that point – this has to do with **causality**. More explicitly, because the wavepacket travels at speed v_g , we have

$$\text{time delay } \Delta t = 2\hbar \frac{d\delta(E)}{dE} \gtrsim -\frac{2R}{v_g}$$

(\gtrsim instead of \geq because our argument isn't completely rigorous here, and it does turn out there's a bit of a correction we need to make), and this rearranges to (because $\frac{dE}{dk} = \frac{\hbar^2 k}{m} = \hbar v_g$)

$$2\hbar \frac{1}{\frac{dE}{dk}} \frac{d\delta}{dk} = 2\hbar \frac{1}{\hbar v_g} \frac{d\delta}{dk} \gtrsim -\frac{2R}{v_g} \implies \boxed{\frac{d\delta}{dk} \gtrsim -R}$$

On the other hand, we may ask whether we can have an arbitrarily **positive** time delay, and this time the answer turns out to be **yes**. We know that if we have a positive potential V_0 in the range $0 < x < R$, that will delay particles of energy $E > V_0$, but that isn't very special because it will also advance particles with energy $E < V_0$ (they will reflect off of the barrier). So what we really need to do is to trap the particle in the potential:

Example 129

Consider a potential of the form

$$V(x) = \begin{cases} \infty & x < 0, \\ -V_0 & 0 < x < a, \\ V_1 & a < x < 2a, \\ 0 & x > 2a, \end{cases}$$

where $V_0, V_1 > 0$. This potential will have states of energy $0 < E < V_1$ which look like bound states but will instead act as resonances with very large time delay.

We've done problems like this before, so we'll skip some of the calculation – qualitatively the solution is exponentially decaying in the region $a < x < 2a$ and sinusoidally oscillating in the others. The relevant constants are then

$$k^2 = \frac{2mE}{\hbar^2}, \quad (k')^2 = \frac{2m(E + V_0)}{\hbar^2}, \quad \kappa^2 = \frac{2m(V_1 - E)}{\hbar^2}.$$

Conceptually, we imagine that the wavepacket will come into the potential, spend a lot of time “bouncing” in the region $0 < x < a$, before finally bouncing out – this will correspond to a very large amplitude for the wavefunction probability density in that region. So in our ansatz

$$\psi(x) = \begin{cases} A \sin(k'x) & 0 < x < a, \\ (?) & a < x < 2a, \\ e^{i\delta} \sin(kx + \delta) & x \geq 2a, \end{cases}$$

we will try to find what values of k make A very large. Within the middle region $a < x < 2a$, we can either use $e^{i\kappa x}$ and $e^{-i\kappa x}$, or we can use $\cosh(\kappa x)$ and $\sinh(\kappa x)$. But a third choice is easiest for imposing boundary conditions, namely $\sinh(\kappa(x - a))$ and $\cosh(\kappa(x - a))$ (we can check that each of these are also linear combinations of the original

exponentials and are solutions to the Schrodinger equation in this region). Since $\cosh(0) = 1$ and $\sinh(0) = 0$, our solution must look like

$$\psi(x) = \begin{cases} A \sin(k'x) & 0 < x < a, \\ A \sin(k'a) \cosh(\kappa(x-a)) + B \sinh(\kappa(x-a)) & a < x < 2a, \\ e^{i\delta} \sin(kx + \delta) & x \geq 2a. \end{cases}$$

We now just need to pick A , B , and δ so that ψ and ψ' are continuous at $x = a$ and $x = 2a$ (we already ensured continuity of ψ at a). It turns out that the relation between all of our variables is

$$\tan(2ka + \delta) = \frac{k}{\kappa} \cdot \frac{\sin(k'a) \cosh(\kappa a) + \frac{k'}{\kappa} \cos(k'a) \sinh(\kappa a)}{\sin(k'a) \sinh(\kappa a) + \frac{k'}{\kappa} \cos(k'a) \cosh(\kappa a)}$$

(the numerator and denominator are just slight rearrangements of each other). Rewriting this in terms of unitless quantities, we will define

$$u = ka, \quad z_0^2 = \frac{2mV_0 a^2}{\hbar^2}, \quad z_1^2 = \frac{2mV_1 a^2}{\hbar^2},$$

so that the unit-free energy (comparing the energy of our packet to the height V_1 of the tall barrier) can be written as

$$e = \frac{E}{V_1} = \frac{\hbar^2 k^2 a^2}{2mV_1 a^2} = \frac{u^2}{z_1^2}.$$

We can also write the other quantities here in terms of u , namely

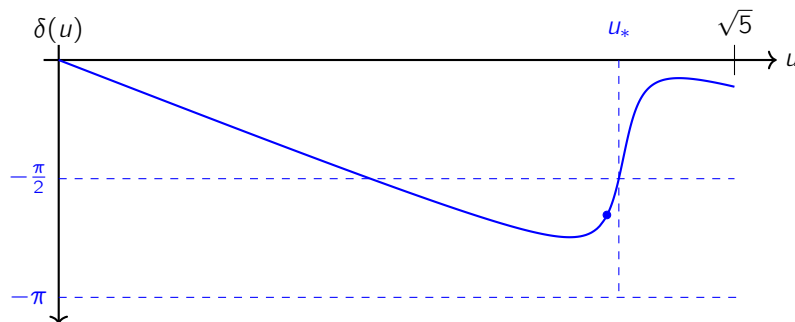
$$(k'a)^2 = u^2 + z_0^2, \quad (\kappa a)^2 = z_1^2 - u^2.$$

So if we're given a fixed potential (in particular the values of a , V_0 , and V_1), the right-hand side now becomes a function of u , because z_0 and z_1 just become numbers. We can then vary u to see the behavior of δ – it's messy, but we can do it in principle.

Example 130

For a numerical example, let's consider $z_0^2 = 1$ and $z_1^2 = 5$, and we'll plot δ as a function of u (which must range between 0 and $z_1 = \sqrt{5}$ if we are indeed looking at energies $0 < E < V_1$).

The dot on the curve below indicates the point where $\tan(2ka + \delta) = 0$, and $u_* \approx 1.8523$ marks the point where δ crosses $-\frac{\pi}{2}$ for the second time (scaling on the x -axis is 4 times larger than on the y -axis):



The slope of this graph is about -2 for small u , because for low energies the tall barrier will essentially make the packet bounce back at $x = a$ instead of $x = 0$, and the delay is proportional to the derivative $\frac{d\delta}{du}$. But at a certain

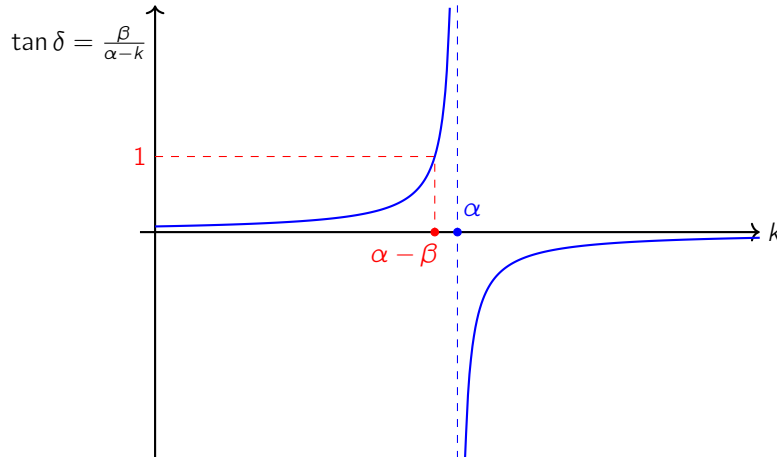
point around u_* , δ jumps very quickly. If we then plot $\sin^2 \delta$, the amplitude of the scattered wave $|A_s^2|$ will peak around the two values where $\delta = -\frac{\pi}{2}$, and will do so more sharply at u_* .

However, the first point where $\delta = -\frac{\pi}{2}$ is not very notable – since the derivative of δ is negative (and not very large), this corresponds to a **time advance**, and we've already discussed above that Δt cannot be very negative. On the other hand, the peak of $|A_s^2|$ at u_* instead corresponds to a **time delay** in which the particle gets trapped in the barrier – this is the resonance that we're looking for. So if we look at the overall delay, which is proportional to the derivative $\frac{d\delta}{du}$, it will be negative for small u , sharply peaking to a large positive value around u_* , and then returning to being slightly negative. And for basically the same reasons, if we plot the amplitude $|A|$ of the wavefunction inside the well, we will see a huge jump (to around 3) when $u \approx u_*$ and not anywhere else.

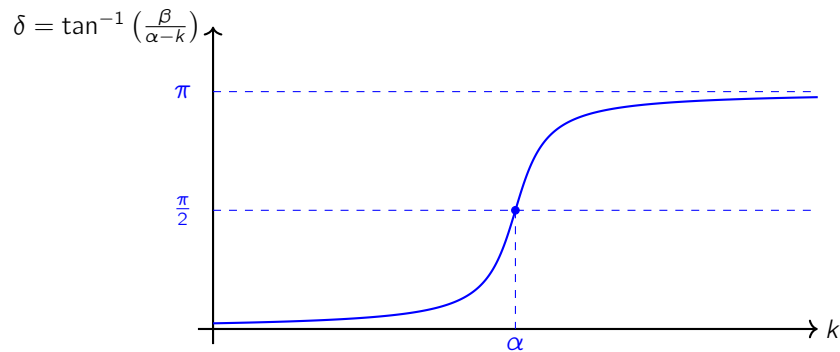
We can now ask how we could solve for resonances like this more mathematically, and we'll do this by modeling what a resonance near some point $k = \alpha$ would look like. We claim that the graph of δ (as a function of k) typically looks something like

$$\tan \delta = \frac{\beta}{\alpha - k} \iff \delta = \tan^{-1} \frac{\beta}{\alpha - k}$$

around $k = \alpha$, for some $\beta > 0$. This is reasonable, because we get a large value of $\sin^2 \delta$ around $\delta = \frac{\pi}{2}$, and $\frac{\beta}{\alpha - k}$ goes to $\pm\infty$ around $k = \alpha$. Specifically, as $k \rightarrow \alpha^-$, $\tan \delta \rightarrow \infty$, and we can characterize how quickly it goes to ∞ by noting that $\frac{\beta}{\alpha - k} = 1$ when $k = \alpha - \beta$:



Similarly, $\tan \delta$ reaches -1 at $k = \alpha + \beta$, so most of the action in δ is happening within a narrow band of width 2β . So to get sharp behavior (and strong resonance), we must set up the system to have β small. If we then plot δ (remember that we choose the multiple of π in arctan so that δ is continuous), we'll see that it is exhibiting the correct behavior as well:



We can then calculate some relevant quantities for this modeled resonance:

$$\left. \frac{d\delta}{dk} \right|_{k=\alpha} = \frac{1}{\beta}, \quad |\psi_s|^2 = |A_s|^2 = \sin^2 \delta = \frac{\beta^2}{\beta^2 + (\alpha - k)^2}$$

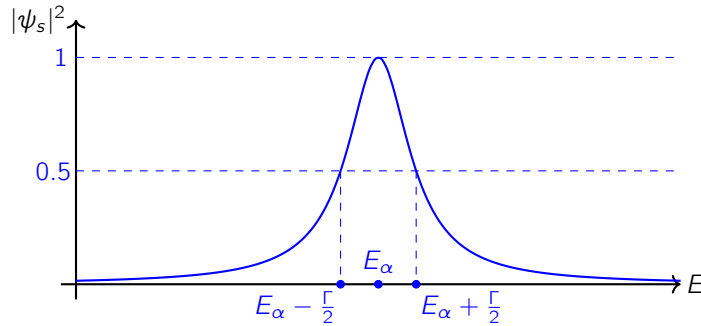
The derivative here makes sense because the phase is changing by almost π over a length scale of β , and the function for the amplitude is actually the famous (non-relativistic) **Breit-Wigner** (also **Cauchy** or **Lorentzian**) distribution, usually written in terms of energy rather than momentum. If we let E_α be the energy of a particle at $k = \alpha$, we'll **make the approximation**

$$E - E_\alpha = \frac{\hbar^2 k^2}{2m} - \frac{\hbar^2 \alpha^2}{2m} = \frac{\hbar^2}{2m}(k^2 - \alpha^2) = \frac{\hbar^2}{2m}(k - \alpha)(k + \alpha) \approx \frac{\hbar^2}{2m}(k - \alpha) \cdot 2\alpha = \frac{\hbar^2 \alpha}{m}(k - \alpha).$$

Substituting this in, we get the formula (now written in the conventional notation) for the squared magnitude of the scattered wave:

$$|\psi_s|^2 = \frac{\frac{1}{4}\Gamma^2}{(E - E_\alpha)^2 + \frac{1}{4}\Gamma^2}, \quad \Gamma = \frac{2\alpha\beta\hbar^2}{m}.$$

Here, Γ is the “full width at half maximum” of the distribution, which is distance between the two points on the curve where $|\psi_s|^2 = 0.5$:



Looking more at the physical significance of $\Gamma = \frac{2\alpha\beta\hbar^2}{m}$, we notice that it has units of energy, so we can get a characteristic time

$$\tau = \frac{\hbar}{\Gamma} = \frac{m}{2\alpha\beta\hbar}.$$

If we then compare this time to the time delay we've been studying,

$$\Delta t = 2\hbar \frac{d\delta}{dE} = 2\hbar \frac{dk}{dE} \frac{d\delta}{dk},$$

and now because (**at resonance** $k = \alpha$) we have $\frac{d\delta}{dk} = \frac{1}{\beta}$ and $\frac{dk}{dE} = \frac{1}{\frac{dE}{dk}} = \frac{1}{\hbar^2 \alpha / m}$, substituting in gives us

$$\Delta t = 2\hbar \frac{m}{\hbar^2 \alpha \beta} = \frac{2m}{\alpha \beta \hbar^2} = 4 \frac{\hbar}{\Gamma} = 4\tau.$$

In other words, the half-width of the scattering distribution gives us a characteristic energy, which is associated with a characteristic time that is related to the physical time delay of the scattering problem! So the larger the time-delay, the smaller our width Γ , and the more sharply peaked our distribution will be. (And this corresponds to δ changing very rapidly around $k = \alpha$.)

Fact 131

This kind of analysis is used in nuclear and particle physics – the Higgs boson is an unstable particle which decays very quickly, but it stays within the potential well during its lifetime (about 10^{-22} seconds). So its cross-section is governed by resonances, and that's a more accurate description than really thinking of it as a particle. We can then observe that the Higgs boson has a central energy around $E_\alpha \approx 125$ GeV and a width of $\Gamma \approx 4$ MeV (to about 5 percent accuracy). So we have a very narrow resonance, and the corresponding time Δt indeed turns out to be around 10^{-22} seconds with those numbers! So the discovery of the Higgs boson had to do with observing that a resonance did occur at this particular energy.

In summary, we find that we cannot have long time advances, but that long time delays can occur in situations of resonance (rapid positive changes of δ). We'll go a little further to put this topic into a more intriguing footing: we can rewrite the scattering amplitude as

$$A_s = \sin \delta e^{i\delta} = \frac{\sin \delta}{e^{-i\delta}} = \frac{\sin \delta}{\cos \delta - i \sin \delta} = \frac{\tan \delta}{1 - i \tan \delta}.$$

If we want this amplitude to be large, we can say that setting $\tan \delta = -i$ would make A_s infinite. Since δ is a phase shift, $\tan \delta$ is always real and it doesn't seem to make sense to set it equal to $-i$. However, we can imagine phase shifts as living in the complex plane, and the idea is that a real phase near an imaginary number with large A_s will also give a large amplitude. To make this more precise, let's plug in the $\tan \delta$ that we've been modeling:

$$A_s = \frac{\frac{\beta}{\alpha - k}}{1 - \frac{i\beta}{\alpha - k}} = \frac{\beta}{\alpha - k - i\beta} = \frac{\beta}{(\alpha - i\beta) - k}.$$

And because we usually plot the scattering amplitude A_s as a function of k , it's nice that we now have an expression in that form, and we can now imagine **plotting A_s in the complex k -plane**. We designed our model so that the resonance occurs at $k = \alpha$, but A_s really becomes infinitely large when $k = \alpha - i\beta$, rather than when $k = \alpha$. (In complex analysis, this is referred to as a **pole**.) So because we have a pole at $\alpha - i\beta$, we'll have large values of A_s near that pole.

So this is how we mathematically search for resonances: if we have a formula for $\delta(k)$, then we can search for solutions to the equation $\tan \delta(k) = -i$. The real part of that solution k will then be the resonance α , and the smaller the imaginary part of k , the more resonant our system actually is.

This viewpoint is additionally interesting because in the formula $E = \frac{\hbar^2 k^2}{2m}$, we can now imagine plugging in a pure imaginary $k = i\kappa$ (for some real number $\kappa > 0$). Then we now have a negative energy $E = -\frac{\hbar^2 \kappa^2}{2m}$, which can instead represent **bound states** of our potential! So the complex k -plane has room for bound states, scattering states, and resonances, and in fact bound states will correspond to poles of A_s as well. We can even go a bit further and invent **anti-bound states** on the negative imaginary axis, in which instead of matching our solution to a purely decaying exponential in the forbidden region, we match it to a purely increasing exponential, and this turns out to actually have applications in nuclear physics!

Lecture 20: Central Potentials and Angular Momentum

We'll now turn our attention fully to three-dimensional quantum mechanics, in particular starting a study of **angular momentum**. Just like position, momentum, or energy, angular momentum is an observable, and we will explore many useful properties of it soon.

Our starting point today is that there is a certain **active view of observables** that we haven't explored much yet. Specifically, we've learned that the momentum operator $\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$ can be thought of as a differential operator (an x-derivative) which tells us how a function varies. In fact, this can be rephrased to saying that the momentum operator actually generates translations and moves functions in space, and the way it generates translations (and the universal trick with Hermitian operators) is to **exponentiate it**. If we want to exponentiate \hat{p} , we need to make it unitless, and we'll do this by considering the operator $e^{\frac{i\hat{p}a}{\hbar}}$ for some length a . Having this act on a wavefunction $\psi(x)$ then yields

$$e^{\frac{i\hat{p}a}{\hbar}} \psi(x) = e^{a \frac{\partial}{\partial x}} \psi(x) = \sum_{n=0}^{\infty} \frac{1}{n!} \left(a \frac{d}{dx} \right)^n \psi(x) = \psi(x) + a \frac{d\psi}{dx} + \frac{a^2}{2!} \frac{d^2\psi}{dx^2} + \frac{a^3}{3!} \frac{d^3\psi}{dx^3} + \dots = \psi(x+a).$$

So this exponential operator takes $\psi(x)$ and translates it, and this characterization of momentum as a "generator of translations" is in some ways more fundamental than what we've already discussed! And similarly, angular momentum will then end up being a "generator of **rotations**" instead, but we'll need a bit more mathematics to discuss it.

There's another story as well – we'll see as the class progresses that angular momentum represents not just physical rotations but also **spin angular momentum** (the mysterious property that particles can have angular momentum without actually rotating). But let's start from the beginning with the setup. As we've been mentioning throughout this class, many of the objects we work with in one dimension generalize to three dimensions as well: for example, the momentum operator becomes

$$p_x = \frac{\hbar}{i} \frac{\partial}{\partial x}, \quad p_y = \frac{\hbar}{i} \frac{\partial}{\partial y}, \quad p_z = \frac{\hbar}{i} \frac{\partial}{\partial z} \implies \vec{p} = \frac{\hbar}{i} \vec{\nabla},$$

, with the commutators $[x, p_x] = [y, p_y] = [z, p_z] = i\hbar$. The time-independent Schrodinger equation then becomes

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

for a three-dimensional vector \vec{r} , where we are trying to find an energy eigenstate $\psi(\vec{r})$ of energy E .

In this class, we'll simplify the problem to the case where we have a **central potential** (in other words, spherically symmetric and invariant under rotations) which only depends on the magnitude of r :

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

This is a strong assumption, but it is the setting of many three-dimensional problems that we will face, and the simplification allows angular momentum to play a role (because "angular momentum generates rotations"). And having a central potential simplifies our calculations, because the Laplacian ∇^2 in spherical coordinates looks like

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

Our goal today will basically be to build up a structure that allows us to ignore the second term with the angular derivatives. It turns out that we can treat the expression

$$-\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)$$

as the **differential version of angular momentum** (much like $\frac{\hbar}{i} \frac{\partial}{\partial x}$ was the differential version of momentum), And it makes sense that this expression instead represents **squared angular momentum** for a variety of reasons: to make the units match up (since \vec{L} should have units of \hbar), because angular momentum should be a first-order derivative ($\vec{r} \times \vec{p}$ involves one derivative) while there is a second-order derivative in the expression above, and because angular momentum is supposed to be a vector. This will end up being the operator \vec{L}^2 .

Fact 132

The main 3-D system we're going to be discussing in the remainder of this course is the **hydrogen atom**, which is a system of two particles. We'll justify (next lecture) that the Schrodinger equation above is relevant in a two-body problem with potential only depending on distance $|\vec{x}_1 - \vec{x}_2|$, so we can reduce the two-body problem (in general) to a one-body problem with a spherically symmetric potential.

For now, we'll focus on developing the theory of angular momentum operators. Since we have $\vec{L} = \vec{r} \times \vec{p}$ classically, we can make an analogous definition quantum mechanically (which will turn out to be good):

Definition 133

The angular momentum operators are defined in the cyclic manner

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \quad \hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z, \quad \hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x.$$

(Notice that because position and momentum operators in different directions commute, it doesn't matter whether we write $\hat{y}\hat{p}_z$ or $\hat{p}_z\hat{y}$, and so on.) These angular momentum operators are Hermitian, because

$$\hat{L}_x^\dagger = \hat{p}_z^\dagger \hat{y}^\dagger - \hat{p}_y^\dagger \hat{z}^\dagger,$$

but all operators on the right-hand side are Hermitian so the daggers go away, and then we can switch the order back to the original order by commutativity. So $\hat{L}_x^\dagger = \hat{L}_x$, and \hat{L}_x is Hermitian (similar logic works for the other two operators). In other words, the operators \hat{L}_i s must be observables, but they'll turn out to be not so simple in certain ways.

Our first step once we define quantum operators is often to compute their commutators: first, let's compute

$$[\hat{L}_x, \hat{L}_y] = [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z].$$

We start by looking at the first term in the first argument, $\hat{y}\hat{p}_z$. Because \hat{y} commutes with everything in the second argument, and \hat{p}_z only has a nonzero commutator with \hat{z} , the only nonzero commutator here is $[\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] = \hat{y}[\hat{p}_z, \hat{z}]\hat{p}_x = -i\hbar\hat{y}\hat{p}_x$. (Here, we're using properties that simplify expressions of the form $[A, BC]$ and $[AB, C]$ – we can check these steps more carefully as an exercise.) Similarly, the only nonzero commutator coming from $-\hat{z}\hat{p}_y$ is $[-\hat{z}\hat{p}_y, -\hat{x}\hat{p}_z] = \hat{p}_y[\hat{z}, \hat{p}_z]\hat{x} = i\hbar\hat{p}_y\hat{x}$, meaning that

$$[\hat{L}_x, \hat{L}_y] = i\hbar(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) = i\hbar\hat{L}_z.$$

So even though there were a lot of terms in the commutator, the end result simplifies very nicely! It turns out this is not that miraculous – if we have symmetry transformations and take their commutator, we must get a symmetry back. (And for some classical intuition, we know that when we rotate in different directions, the order does matter, so this commutator should be nonzero.) Furthermore, because we defined our angular momentum operators in a cyclic way, we must also have

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

These relations give us the **quantum algebra of angular momentum**, and this algebra in fact appears in many different fields of mathematics and physics – it's related to the algebra of generators of the special unitary group $SU(2)$, as well as the orthogonal group of rotations $O(3)$. So the structure is universal and deeper than the derivation – if there are other sets of operators which satisfy these commutation relations but don't come from \hat{x} s and \hat{p} s, they can still be

angular momentum operators, and that is in fact what happens with **spin** (in which we have $[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z$ and so on).

Fact 134

Mathematicians approach this topic as the study of **Lie algebras**, and the job there is basically to classify all potential consistent commutation relations – the one we’ve described is the simplest nontrivial one.

Since we have observables, it now makes sense to ask whether we can actually “observe” them, in the sense that there is a state with a definite value of \hat{L}_x , \hat{L}_y , or L_z . Recall that because position and momentum do not commute, we cannot tell simultaneously the values of both at once. And these angular momentum operators don’t commute either, so **we basically cannot have simultaneous eigenstates** of \hat{L}_x , \hat{L}_y , and L_z . More rigorously, suppose that we have a simultaneous eigenstate ϕ_0 of \hat{L}_x and \hat{L}_y , with corresponding eigenvalues λ_x and λ_y . Then

$$\hat{L}_x\hat{L}_y\phi_0 = \hat{L}_x(\lambda_y\phi_0) = \lambda_x\lambda_y\phi_0, \quad \hat{L}_y\hat{L}_x\phi_0 = \hat{L}_y(\lambda_x\phi_0) = \lambda_x\lambda_y\phi_0,$$

so subtracting yields $[\hat{L}_x, \hat{L}_y]\phi_0 = 0 \implies i\hbar\hat{L}_z\phi_0 = 0$. This means that ϕ_0 is then also an eigenstate of \hat{L}_z with $\lambda_z = 0$. But now that we’re an eigenstate of all three operators, applying the same logic to a different commutator then tells us that $\lambda_x = \lambda_y = 0$ as well, so the only way to be a simultaneous eigenstate is if ϕ_0 is killed by all of the operators \hat{L}_x , \hat{L}_y , and \hat{L}_z , which is not very interesting. Thus, **no state is a nontrivial eigenstate of two angular momentum operators**, and we can only ever “measure” one of the values of \hat{L}_x , \hat{L}_y , and \hat{L}_z at a given time.

But it is possible to know more about the state, and this basically comes down to thinking of another operator that commutes with all of \hat{L}_x , \hat{L}_y , and \hat{L}_z (meaning that it must be rotationally invariant). And this is now connected to an object we introduced earlier in the lecture:

Definition 135

The operator \vec{L}^2 is defined to be

$$\vec{L}^2 = \hat{L}_x\hat{L}_x + \hat{L}_y\hat{L}_y + \hat{L}_z\hat{L}_z.$$

It turns out that this definition is equivalent to the $-\hbar^2 \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right)$ mentioned above, but we’ll work with the more algebraic definition for now. In particular (just doing a direct computation),

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

(Remember that we can move constants around but should not switch the order of the angular momentum operators.) And now the first and last terms cancel, as do the second and third, and thus \hat{L}_x and \vec{L}^2 commute, meaning that **it is possible to be a simultaneous eigenstate of both operators!** And similarly, \vec{L}^2 then commutes with \hat{L}_y and \hat{L}_z as well.

Fact 136

We’ll see more of this in 8.05, but it turns out (by linear algebra) that for any two commuting Hermitian operators, we can always find simultaneous eigenstates of both operators. (The reason for wanting simultaneous eigenstates is to discover more specific information about our states, and so we will generally aim for the **maximal set of commuting operators**.)

Returning to coordinates now, remembering that in spherical coordinates we have

$$x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi, \quad z = r \cos \theta,$$

and thus we can also invert these equations to find

$$r = \sqrt{x^2 + y^2 + z^2}, \quad \theta = \cos^{-1} \frac{z}{r}, \quad \phi = \tan^{-1} \frac{y}{x},$$

and the special role that z plays (over x and y) means that the angular momentum operator \hat{L}_z looks the nicest in spherical coordinates, because rotations about z don't change the value of ϕ . In particular, the multivariable chain rule tells us that

$$\frac{\partial}{\partial \phi} = \frac{\partial y}{\partial \phi} \frac{\partial}{\partial y} + \frac{\partial x}{\partial \phi} \frac{\partial}{\partial x} + \frac{\partial z}{\partial \phi} \frac{\partial}{\partial z}.$$

The last term is zero because z doesn't depend on ϕ , and we can compute the derivatives of x and y with respect to ϕ : we have $\frac{\partial y}{\partial \phi} = r \sin \theta \cos \phi = x$, and similarly $\frac{\partial x}{\partial \phi} = -y$, so

$$\frac{\partial}{\partial \phi} = x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}.$$

Remembering that momentum operators are differential operators, we thus see that $\hat{L}_z = \frac{\hbar}{i} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$, meaning that $\hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$ in spherical coordinates! (The units of this expression are correct, because angles have no units and angular momentum should have units of \hbar .) And using this kind of technique (but more work), we can also get expressions for \hat{L}_x , \hat{L}_y , and \vec{L}^2 , the latter of which agrees with our expression above. So the angular momentum operator does indeed relate to the angular component of the Laplacian.

Turning our attention back now to **simultaneous eigenstates**, we now wish to construct functions which are eigenstates of both \vec{L}^2 and one of \vec{L}_x , \vec{L}_y , and \vec{L}_z . (For such functions, the angular part of the Laplacian is just a number, which will allow us to simplify the process of solving the Schrodinger equation to just solving a differential equation for the radial component.) Because \hat{L}_z looks simple in spherical coordinates, we always choose \hat{L}_z instead of the others by convention.

We'll denote the eigenstate $\psi_{\ell,m}(\theta, \phi)$ for some numbers ℓ, m related to the eigenvalues (which are currently arbitrary). Since \hat{L}_z should have units of \hbar , it makes sense to require that

$$\hat{L}_z \psi_{\ell,m} = \hbar m \psi_{\ell,m}$$

for some real number m . Similarly, since \vec{L}^2 should have units of \hbar^2 , we'll require that

$$\vec{L}^2 \psi_{\ell,m} = \hbar^2 \lambda \psi_{\ell,m}$$

for some real number λ . Additionally, λ **must be positive** because \vec{L}^2 is a positive operator; specifically,

$$\begin{aligned} \hbar^2 \lambda (\psi_{\ell,m}, \psi_{\ell,m}) &= (\psi_{\ell,m}, \vec{L}^2 \psi_{\ell,m}) = (\psi_{\ell,m}, \hat{L}_x \hat{L}_x \psi_{\ell,m}) + (\psi_{\ell,m}, \hat{L}_y \hat{L}_y \psi_{\ell,m}) + (\psi_{\ell,m}, \hat{L}_z \hat{L}_z \psi_{\ell,m}) \\ &= (\hat{L}_x \psi_{\ell,m}, \hat{L}_x \psi_{\ell,m}) + (\hat{L}_y \psi_{\ell,m}, \hat{L}_y \psi_{\ell,m}) + (\hat{L}_z \psi_{\ell,m}, \hat{L}_z \psi_{\ell,m}). \end{aligned}$$

The right-hand side is now nonnegative (because we're calculating a squared norm), so the left-hand side must be nonnegative as well, meaning $\lambda \geq 0$. Anticipating this, we will actually write

$$\vec{L}^2 \psi_{\ell,m} = \hbar^2 \ell(\ell + 1) \psi_{\ell,m}$$

for some real number $\ell \in \mathbb{R}$ – this exact choice will make sense very soon as we return to the differential equation, and we’re not losing any generality here because $\ell(\ell + 1)$ can take on any nonnegative real value (and even some negative ones). In fact, because the range of $\ell(\ell + 1)$ over nonnegative ℓ is $[0, \infty)$, we can always **pick ℓ to be nonnegative**.

We’ll now solve the two boxed differential equations to work towards an explicit formula for $\psi_{\ell,m}$. To satisfy the first equation, we must have

$$\frac{\hbar}{i} \frac{\partial}{\partial \phi} \psi_{\ell,m} = \hbar m \psi_{\ell,m} \implies \frac{\partial}{\partial \phi} \psi_{\ell,m} = im \psi_{\ell,m} \implies \psi_{\ell,m}(\theta, \phi) = e^{im\phi} P_{\ell}^m(\theta)$$

for some arbitrary function P_{ℓ}^m . So the ϕ -dependence is not complicated if our state is an eigenstate of \hat{L}_z , but we can actually say a bit more – we must have $\psi_{\ell,m}(\theta, \phi + 2\pi) = \psi_{\ell,m}(\theta, \phi)$, because ϕ is a coordinate that is only defined modulo 2π anyway. Thus we must require $e^{2im} = 1$, or in other words that m **must be an integer**. So the eigenvalues of \hat{L}_z actually need to be quantized – they can only be integer multiples of \hbar .

For the second equation, a bit more work needs to be done. Substituting in the expression for \hat{L}^2 , we have

$$-\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \psi_{\ell,m} = \hbar^2 \ell(\ell + 1) \psi_{\ell,m}.$$

We already know how the $\frac{\partial^2}{\partial \phi^2}$ acts on $\psi_{\ell,m}$ (each derivative contributes an im factor), and then the \hbar^2 s and $e^{im\phi}$ s on both sides cancel out. Further multiplying by $-\sin^2 \theta$, we are instead solving the differential equation

$$\left(\sin \theta \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} - m^2 \right) P_{\ell}^m = -\ell(\ell + 1) \sin^2 \theta P_{\ell,m}.$$

Remember that $\sin \theta \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta}$ means that we apply these operators from right to left, so applying them on P_{ℓ}^m is really $\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{dP_{\ell}^m}{d\theta} \right)$. So moving everything to one side, and remembering that P is just a function of a single variable, we wish to find solutions to

$$\boxed{\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{dP_{\ell}^m}{d\theta} \right) + [\ell(\ell + 1) \sin^2 \theta - m^2] P_{\ell}^m = 0.}$$

This equation has been studied extensively (because it comes up when we are studying the Laplacian), and one useful parameter substitution to use is to have the variable $x = \cos \theta$ instead, so that $\frac{d}{dx} = -\frac{1}{\sin \theta} \frac{d}{d\theta}$ and $\sin \theta \frac{d}{d\theta} = -(1-x^2) \frac{d}{dx}$ (we should check this as an exercise). But with these facts, plus the fact that $\sin^2 \theta = 1 - x^2$, our differential equation can be rewritten to **only involve polynomials**: after some simplification (dividing by $(1 - x^2)$), we arrive at

$$\frac{d}{dx} \left[(1 - x^2) \frac{dP_{\ell}^m}{dx} \right] + \left[\ell(\ell + 1) - \frac{m^2}{1 - x^2} \right] P_{\ell}^m(x) = 0,$$

where our (now normalized) simultaneous eigenstates are $\psi_{\ell,m} = N_{\ell,m} e^{im\phi} P_{\ell}^m(\cos \theta)$ for some numbers $N_{\ell,m}$. This differential equation still looks rather complicated, and the way physicists approach it is usually to start with the $m = 0$ case (where P_{ℓ}^0 is usually just denoted P_{ℓ}):

$$\frac{d}{dx} \left[(1 - x^2) \frac{dP_{\ell}}{dx} \right] + \ell(\ell + 1) P_{\ell}(x) = 0.$$

We can solve this with a series solution: letting $P_{\ell}(x) = \sum_k a_k x^k$ and substituting in, the x^k coefficient gives us the recursion (much like for the harmonic oscillator)

$$(k + 1)(k + 2) a_{k+2} + [\ell(\ell + 1) - k(k + 1)] a_k = 0 \implies \frac{a_{k+2}}{a_k} = -\frac{\ell(\ell + 1) - k(k + 1)}{(k + 1)(k + 2)}.$$

And just like with the harmonic oscillator, if our series solution doesn’t determinate, we’ll get singular solutions diverging

at $x = 1$ or $x = -1$, which is bad (since those points are included in the range of the wavefunction). So **the series must terminate** at some point, and that can only occur if $\ell(\ell + 1) - k(k + 1) = 0$ for some nonnegative integer k . And now we see exactly why we chose this form for the eigenvalue of \vec{L}^2 – since we’re picking ℓ to be nonnegative (as mentioned earlier in the lecture), $\ell = k$ **must be a nonnegative integer**. So $P_\ell(x)$ is a polynomial of degree ℓ (these polynomials are known as the **Legendre polynomials**), and we find **quantization of the eigenvalues of \vec{L}^2** ! In other words, both the angular momentum along the z -direction and the overall magnitude of the angular momentum are quantized. Next lecture, we’ll explore these equations some more, understanding what happens for nonzero m and what additional constraints exist for our operators.

Lecture 21: Spherical Harmonics, Boundary Conditions, and the Hydrogen Atom

Last lecture, we started studying angular momentum by constructing a set of operators that provide observables. Angular momentum becomes particularly important when we have a central potential (only depending on the radial variable r), and we’ll soon use this to help solve the hydrogen atom. But first we’ll review what we discovered last time: the commutators of $\hat{L}_x, \hat{L}_y, \hat{L}_z$ form an algebra of angular momentum, explaining that we cannot have simultaneous eigenstates of these operators. However, we can have simultaneous eigenstates of one of them (we pick \hat{L}_z) with \vec{L}^2 , because $[\vec{L}^2, \hat{L}_z] = 0$, which we denote $\psi_{\ell,m}$. And we calculated last time that the eigenvalues of this state for \hat{L}_z and \vec{L}^2 are of the form $\hbar m$ and $\hbar^2 \ell(\ell + 1)$, respectively, where m is an integer and ℓ is a nonnegative integer.

Remark 137. *In Fact 136, we mentioned that the goal is often to be simultaneous eigenstates of as many operators as possible. One additional point here is that we have succeeded if we can uniquely characterize states using the corresponding observables! For example, we might have multiple degenerate states at the same energy, but they may have different values of ℓ , allowing us to tell them apart by measurement. And there might be degenerate states of the same E and ℓ , but then they may have different values of m . This is important because we want to always be able to tell apart two states with some physical difference, and that’s a setting we will see soon with the hydrogen atom.*

We also started working towards more explicit forms of the $\psi_{\ell,m}$ states at the end of the lecture – last time, we found that for $m = 0$, we have $\psi_{\ell,0} = N_{\ell,m} e^{im\phi} P_\ell(\cos\theta)$, where P_ℓ are the **Legendre polynomials** which turn out to be given by

$$P_\ell(x) = \frac{1}{2^\ell \ell!} \left(\frac{d}{dx} \right)^\ell (x^2 - 1)^\ell.$$

We’ll complete this analysis today, beginning by studying nonzero m in the differential equation for P_ℓ^m . It turns out there is a simple rule for going from the Legendre polynomials to the **Legendre functions**:

$$P_\ell^m(x) = (1 - x^2)^{\frac{|m|}{2}} \left(\frac{d}{dx} \right)^m P_\ell(x)$$

Notice that the exponent of $(1 - x^2)$ can be a half-integer, but this is not actually a problem because $(1 - x^2)$ will become $\sin^2\theta$ when we substitute it back into our coordinates. Checking that this P_ℓ^m solves the differential equation $\frac{d}{dx} \left[(1 - x^2) \frac{dP_\ell^m}{dx} \right] + \left[\ell(\ell + 1) - \frac{m^2}{1 - x^2} \right] P_\ell^m(x) = 0$ takes some work, and we won’t check it here, but what’s important is to notice that **we can only take ℓ derivatives** before $P_\ell(x)$ (a polynomial of degree ℓ) vanishes completely, and thus we must have $|m| \leq \ell \iff -\ell \leq m \leq \ell$.

Fact 138

It turns out that **there are no additional regular (non-divergent) solutions** to the differential equation besides the P_ℓ^m s that we compute here. So this boxed condition is an actual constraint on our quantum numbers for angular momentum – given any magnitude for the angular momentum, there are only certain values for the angular momentum in the z-direction (which makes sense).

In other words, the only state with $\ell = 0$ will also have $m = 0$, but there are three states with $\ell = 1$ (with $m = -1, 0, 1$ respectively), five states with $\ell = 2$ (with $m = -2, -1, 0, 1, 2$ respectively), and so on – in general, there are $2\ell + 1$ states at total angular momentum quantum number ℓ . This leads us back to the final normalized solution that we want:

Theorem 139

The **spherical harmonics** are simultaneous normalized eigenstates of \hat{L}_z and \vec{L}^2 given by

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

when $0 \leq m \leq \ell$ and

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

when $-\ell \leq m \leq 0$.

We can find the explicit formulas for these by looking them up – they are complicated in general, but it's useful to remember the ones for $\ell = 0, 1$:

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}}, \quad Y_{1,\pm 1} = \mp \sqrt{\frac{3}{8\pi}} e^{\pm i\phi} \sin\theta, \quad Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos\theta.$$

And here, normalization means that the spherical harmonics are normalized over all θ, ϕ , so that (integrating over solid angle)

$$\int (Y_{\ell,m}(\theta, \phi))^2 d\Omega = \int_0^\pi \sin\theta \int_0^{2\pi} |Y_{\ell,m}(\theta, \phi)|^2 d\phi d\theta = 1.$$

But we can recognize further that $\sin\theta d\theta = -d(\cos\theta)$, so making a change of variables means that we are requiring

$$\int_{-1}^1 \int_0^{2\pi} |Y_{\ell,m}|^2 d\phi d(\cos\theta) = 1.$$

(We will often represent this double integral by $d\Omega$ to simplify our notation.) And because the different $Y_{\ell,m}$ s are eigenfunctions of operators with (at least one being) different eigenvalues, they must be orthogonal:

$$\int d\Omega Y_{\ell',m'}^*(\theta, \phi) Y_{\ell,m}(\theta, \phi) = \delta_{\ell,\ell'} \delta_{m,m'}.$$

We're now ready to return to the full Schrodinger equation in three dimensions for a central potential, which takes the form

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V(r)\psi = E\psi.$$

Plugging in the form of the Laplacian in spherical coordinates, including the definition of \vec{L}^2 , we now have

$$-\frac{\hbar^2}{2m} \left[\frac{1}{r} \frac{d^2}{dr^2} r\psi - \frac{1}{\hbar^2 r^2} \vec{L}^2 \psi \right] + V(r)\psi = E\psi.$$

(Notice that \vec{L}^2 and $\frac{1}{r^2}$ commute, because the former only involves θ and ϕ , so we don't have to worry about the ordering there. And if we want, we can prove that $[\vec{L}^2, \hat{r}] = 0$ by direct calculation as well, but that's more work.) So now we can make the most important simplification: **try a factorized solution** of the form

$$\psi(\vec{r}) = R_E(r)Y_{\ell,m}(\theta, \phi).$$

Plugging this solution in, \vec{L}^2 will just act as a number on ψ (because we have an angular momentum eigenstate), so there will be a factor of $Y_{\ell,m}$ that we can cancel everywhere, leaving us with

$$-\frac{\hbar^2}{2m} \left[\frac{1}{r} \frac{d^2}{dr^2} (rR_E(r)) - \frac{\ell(\ell+1)}{r^2} R_E(r) \right] + V(r)R_E(r) = ER_E(r).$$

So we now just need to solve a one-variable differential equation for $R_E(r)$, and then multiplying by a spherical harmonic will give us a solution to the Schrodinger equation with energy E , angular momentum ℓ , and z-component of angular momentum m . To make that easier, we'll clean it up by multiplying everything by r :

$$-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} (rR_E(r)) + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2} (rR_E(r)) + V(r)(rR_E(r)) = E(rR_E(r)).$$

Defining $U(r) = rR_E(r)$, we find that the differential equation we actually need to solve is

$$\boxed{-\frac{\hbar^2}{2m} \frac{d^2 U(r)}{dr^2} + \left(V(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} \right) U(r) = EU(r)}.$$

So the radial equation turns out to just be exactly like a **a one-dimensional Schrodinger equation**, except the radial dependence needs to be obtained by dividing through by r to get to $R_E(r)$, and we need to solve the equation repeatedly for all values of ℓ . We can basically think of this additional term $\frac{\hbar^2 \ell(\ell+1)}{2mr^2}$ as a **centrifugal barrier**, making it harder to reach the origin, so we now have an **effective radial potential**

$$\boxed{V_{\text{eff}}(r) = V(r) + \frac{\hbar^2}{2mr^2} \ell(\ell+1)}$$

taking the usual place of $V(r)$. And notice that even for a Coulomb potential $V(r) \propto \frac{1}{r}$, the second term will dominate near $r = 0$ for any nonzero ℓ , meaning that a particle with any nonzero angular momentum cannot reach the origin (intuitively because it must spin faster and faster). And now that we're in the one-dimensional setting, many of the properties and theorems we've discovered previously in the class (about bound states and eigenstates and so on) suddenly become useful. Our full wavefunctions are thus of the form $\psi(\vec{r}) = \frac{U(r)}{r} \psi_{\ell,m}(\theta, \phi)$, and we can notice that $U(r)$ **depends on ℓ but does not depend on m** – the m -dependence in this wavefunction is really only showing up in the spherical harmonic. (And we can write $U_{E,\ell}(r)$ to represent this.)

We've talked about normalization for the spherical harmonics, but now we need to ask about normalization for the full wavefunction: we have that

$$1 = \int |\psi|^2 d^3x = \int_0^\infty \int \frac{|U(r)|^2}{r^2} |Y_{\ell,m}(\theta, \phi)|^2 r^2 dr d\Omega.$$

But the r^2 factors will cancel, and the solid angle integral $\int |Y|^2 d\Omega$ is just one by normalization of spherical harmonics, and therefore everything simplifies to

$$1 = \int_0^\infty |U(r)|^2 dr.$$

So we truly can think of this as a one-dimensional problem – the normalization condition for ψ is just the usual one-dimensional normalization condition for U ! This means that we're successful, and we've reduced a spherical potential

to a one-dimensional problem.

There is an additional difference, though – because r only runs over the positive reals, we might ask if there are boundary conditions that need to be satisfied as $r \rightarrow 0$. Our argument here will not be completely general, but it will be good enough – for any potential $V(r)$ where the centrifugal barrier $\frac{\hbar^2 \ell(\ell+1)}{2mr^2}$ dominates as $r \rightarrow 0$ (such as the Coulomb potential), our differential equation will become

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} u \approx 0 \implies \frac{d^2 u}{dr^2} \approx \frac{\ell(\ell+1)}{r^2} u$$

to leading order. This is essentially a Cauchy-Euler equation, and the solutions are proportional to $r^{\ell+1}$ or $r^{-\ell}$. But the latter can be ruled out – it's not normalizable for $\ell \geq 1$, and for $\ell = 0$ we can't actually have a valid exact solution to the Schrodinger equation (though we won't talk about this in full detail). So instead we must have

$$U(r) \sim r^{\ell+1} \text{ as } r \rightarrow 0,$$

and in particular $U(r)$ always vanishes as $r \rightarrow 0$ for any ℓ , vanishing faster and faster for higher values of ℓ . So this is consistent with imagining an infinite barrier at $r = 0$.

With all of the theory set up, we're now ready to attack the main problem we'd like to solve:

Example 140

Consider a proton (of position and momentum \vec{x}_p and \vec{p}_p , respectively) and electron (of position and momentum \vec{x}_e and \vec{p}_e , respectively), in which we use **canonical variables** for each particle. In other words, we have $[(\vec{x}_p)_i, (\vec{p}_p)_j] = i\hbar\delta_{ij}$ (where i and j range over 1, 2, 3 to represent the x, y, or z-coordinates), and similarly $[(\vec{x}_e)_i, (\vec{p}_e)_j] = i\hbar\delta_{ij}$.

Since we now have a system of two particles, our wavefunction should account for both, meaning that we now have a function $\Psi(\vec{x}_e, \vec{x}_p)$. The interpretation of this wavefunction is still that the squared wavefunction is the probability density, but specifically

$$dP = |\Psi(\vec{x}_e, \vec{x}_p)|^2 d^3\vec{x}_e d^3\vec{x}_p$$

is the probability that we find the electron in a region $d^3\vec{x}_e$ around \vec{x}_e **and** the proton in a region $d^3\vec{x}_p$ around \vec{x}_p . (So if we just care about the position of the proton, we'd integrate this density out across all $d^3\vec{x}_e$.) And what's important to note here is that there is still only one wavefunction and one Schrodinger equation, even with multiple particles, but this time our Hamiltonian looks a bit more complicated: we have

$$\hat{H} = \frac{(\vec{p}_p)^2}{2m_p} + \frac{(\vec{p}_e)^2}{2m_e} + V(|\vec{x}_e - \vec{x}_p|),$$

because each particle has a kinetic energy and the potential energy between them depends only on their distance. So in our Schrodinger equation $H\psi = E\psi$, we treat \vec{p}_p as taking derivatives of the proton's position and \vec{p}_e as taking derivatives of the electron's position.

But this Schrodinger equation now has a lot of variables, and our goal will be (as we've previously mentioned) to simplify the equation so that it reduces to an equation for the distance between the particles. The **change of variables** we must perform is now motivated by classical mechanics: because the center-of-mass moves at constant velocity in a classical two-body problem, we should also be able to define a new quantum coordinate and momentum for the center-of-mass. So we'll define

$$\vec{P} = \vec{p}_p + \vec{p}_e,$$

and now we need to define a corresponding coordinate \vec{X} – motivated by classical mechanics, we try

$$\vec{X} = \frac{m_p \vec{x}_p + m_e \vec{x}_e}{m_e + m_p}.$$

Now we must check if these are indeed a valid coordinate-momentum pair; in other words, we must check that $[\vec{X}_i, \vec{P}_j] = i\hbar\delta_{ij}$. Indeed, this commutator is

$$\left[\frac{m_p(\vec{x}_p)_i + m_e(\vec{x}_e)_i}{m_e + m_p}, (\vec{p}_p)_j + (\vec{p}_e)_j \right] = \frac{m_p}{m_e + m_p} [(\vec{x}_e)_i, (\vec{p}_e)_j] + \frac{m_e}{m_e + m_p} [(\vec{x}_e)_i, (\vec{p}_e)_j]$$

(since commutators between proton and electron coordinates and momenta are zero), and this is zero unless $i = j$, in which case it is $i\hbar \left(\frac{m_p}{m_e + m_p} + \frac{m_e}{m_e + m_p} \right) = i\hbar$. So yes, this is a valid pair of quantum mechanical canonical variables (they have the right units and commutator). To get a second one, it makes sense to use the **relative coordinate**

$$\vec{x} = \vec{x}_e - \vec{x}_p$$

which appears in our expression for the Hamiltonian. But even when we write this down, we have to be careful – remembering that the variables for the proton and electron commuted, **we must also have that the relative and center-of-mass variables commute with each other**. This does turn out to be the case for \vec{x} with \vec{X} and \vec{P} – all \vec{x} s commute with each other (so there's no problem there), and when taking commutators of \vec{x} with \vec{P} , the negative sign for the proton commutator means that the $i\hbar$ s cancel out. So we just need to define a corresponding combination of the momenta

$$\vec{p} = \alpha \vec{p}_e - \beta \vec{p}_p.$$

This will always commute with \vec{P} , but we need to choose the coordinates so that $[\vec{x}_i, \vec{p}_j] = i\hbar\delta_{ij}$ (this turns out to enforce $\alpha + \beta = 1$) and that all components of \vec{p} commute with \vec{X} (this enforces $\alpha m_e - \beta m_p = 0$). Solving the system of two equations gives us

$$\vec{p} = \frac{m_p}{m_e + m_p} \vec{p}_e - \frac{m_e}{m_e + m_p} \vec{p}_p.$$

So we now have two new pairs of canonical variables, and to make the notation simpler, it's useful to define the **reduced mass** and **total mass**

$$\mu = \frac{m_e m_p}{m_e + m_p}, \quad M = m_e + m_p.$$

(Since we're in a setting where the proton is much heavier than the electron, we'll have $\mu \approx m_e$ and $M \approx m_p$ in this case.) In terms of these variables, we then have the unit-free constants $\alpha = \frac{\mu}{m_e}$ and $\beta = \frac{\mu}{m_p}$, so that another way to write our relative momentum is

$$\vec{p} = \mu \left(\frac{\vec{p}_e}{m_e} - \frac{\vec{p}_p}{m_p} \right).$$

The point of doing all of these calculations is that we want to write the two-body Hamiltonian in terms of our new coordinates. Since \vec{P} and \vec{p} are both linear combinations of \vec{p}_e and \vec{p}_p , we can solve to find that

$$\vec{p}_p = \frac{m_p}{M} \vec{P} - \vec{p}, \quad \vec{p}_e = \frac{m_e}{M} \vec{P} + \vec{p}.$$

And now is where the effort pays off: the kinetic energy terms in the Hamiltonian are

$$\frac{(\vec{p}_p)^2}{2m_p} + \frac{(\vec{p}_e)^2}{2m_e} = \frac{1}{2m_p} \left(\frac{m_p}{M} \vec{P} - \vec{p} \right)^2 + \frac{1}{2m_e} \left(\frac{m_e}{M} \vec{P} + \vec{p} \right)^2,$$

and now the cross-terms vanish: the kinetic energy operator in the Hamiltonian indeed simplifies to

$$\frac{(\vec{p}_p)^2}{2m_p} + \frac{(\vec{p}_e)^2}{2m_e} = \boxed{\frac{1}{2M}\vec{P}^2 + \frac{1}{2\mu}\vec{p}^2},$$

a center-of-mass contribution and a relative contribution. And next lecture, we'll see that this allows us to separate the Schrodinger equation into center-of-mass motion and relative motion, reducing to a one-body problem.

Lecture 22: Solving the Hydrogen Atom

Last lecture, we rewrote the hydrogen atom Hamiltonian operator in terms of two new pairs of canonical variables (center-of-mass and relative position):

$$\hat{H} = \frac{(\vec{p}_p)^2}{2m_p} + \frac{(\vec{p}_e)^2}{2m_e} + V(|\vec{x}_e - \vec{x}_p|) = \frac{1}{2M}\vec{P}^2 + \frac{1}{2\mu}\vec{p}^2 + V(|\vec{x}|).$$

In other words, this Hamiltonian describes a system in which the center-of-mass moves as a free particle of mass $M = m_p + m_e$, and in which the relative position moves as a particle of reduced mass $\mu = \frac{m_e m_p}{m_e + m_p}$ under a central potential V only depending on the magnitude of the distance. But to actually check that, we need to solve the Schrodinger equation, and we have to be a bit careful with the two different coordinates – we have $\vec{P} = \hbar \nabla_{\vec{X}}$ and $\vec{p} = \hbar \nabla_{\vec{x}}$ (gradients must be taken with respect to the corresponding canonical coordinate). So to solve the (time-independent) Schrodinger equation, we'll write down our wavefunction $\psi(\vec{X}, \vec{x})$ in terms of the new coordinates, and we'll do **separation of variables**

$$\psi(\vec{X}, \vec{x}) = \psi_{\text{CM}}(\vec{X})\psi_{\text{rel}}(\vec{x}).$$

Substituting this into $\hat{H}\psi = E\psi$ (grouping the second and third terms of \hat{H} together), we have

$$\left(\frac{1}{2M}\vec{P}^2\psi_{\text{CM}}(\vec{X})\right)\psi_{\text{rel}}(\vec{x}) + \left(\frac{1}{2\mu}\vec{p}^2\psi_{\text{rel}}(\vec{x}) + V(|\vec{x}|\psi_{\text{rel}}(\vec{x})\right)\psi_{\text{CM}}(\vec{X}) = E\psi_{\text{CM}}(\vec{X})\psi_{\text{rel}}(\vec{x})$$

(since \vec{P} only acts on the center of mass and \vec{p} only acts on the relative motion). If we now divide by the total wavefunction $\psi_{\text{CM}}(\vec{X})\psi_{\text{rel}}(\vec{x})$, we have

$$\frac{1}{\psi_{\text{CM}}(\vec{X})} \left(\frac{1}{2M}\vec{P}^2\psi_{\text{CM}}(\vec{X})\right) + \frac{1}{\psi_{\text{rel}}(\vec{x})} \left(\frac{1}{2\mu}\vec{p}^2\psi_{\text{rel}}(\vec{x}) + V(|\vec{x}|\psi_{\text{rel}}(\vec{x})\right) = E.$$

But now the first term depends only on \vec{X} , while the second term depends only on \vec{x} , so the only way their sum can be a constant is if each term is a constant – let's denote those constants E_{CM} and E_{rel} , respectively. So we now have two simpler differential equations to solve, namely (now multiplying back by ψ_{CM} and ψ_{rel} respectively)

$$\frac{1}{2M}\vec{P}^2\psi_{\text{CM}}(\vec{X}) = E_{\text{CM}}\psi_{\text{CM}}(\vec{X}), \quad \frac{1}{2\mu}\vec{p}^2\psi_{\text{rel}}(\vec{x}) + V(|\vec{x}|\psi_{\text{rel}}(\vec{x}) = E_{\text{rel}}\psi_{\text{rel}}(\vec{x}), \quad E = E_{\text{CM}} + E_{\text{rel}}.$$

So we have two time-independent Schrodinger equations for $\psi_{\text{CM}}(\vec{X})$ and $\psi_{\text{rel}}(\vec{x})$, under no potential and the potential $V(|\vec{x}|)$, respectively. But we know how wavefunctions look for a free particle (momentum plane waves), and we have been building up the theory for dealing with a particle in a central potential! So intuitively, a hydrogen atom moves as a free particle, but then the behavior of the electron relative to the proton is governed by some central interaction. We can now start to study the actual potential that we have in a hydrogen atom:

Example 141 (Hydrogen-like atom)

Suppose that instead of a single proton, we have a nucleus of Z protons. Then the potential for the relative motion is given by

$$V(r) = -\frac{Ze^2}{r},$$

where $r = |\vec{x}|$ is the distance between the particles and e is the charge of a proton (remembering that a proton and electron have opposite charge).

The characteristic length scale for this system is the **Bohr radius**, given by setting equal the units from kinetic and potential energy: since $\frac{\hbar}{a_0}$ has units of momentum, we can set equal

$$\frac{\hbar^2}{ma_0^2} = \frac{e^2}{a_0} \implies a_0 = \frac{\hbar^2}{me^2}.$$

Intuitively, the e appears in the denominator here, because the stronger the Coulomb force, the smaller the atom should be (because the electron is more tightly bound). To get a rough estimate of this quantity, we can write

$$a_0 = \frac{\hbar^2 c^2}{e^2 mc^2} = \frac{\hbar c}{\frac{e^2}{\hbar c} \cdot mc^2},$$

and now we use the fact that the **fine structure constant** $\alpha = \frac{e^2}{\hbar c}$ is approximately $\frac{1}{137}$, and we plug in the mass of the electron instead of the reduced mass (it makes only a small percentage difference):

$$= \frac{197 \text{ MeV} \cdot \text{fm}}{\frac{1}{137} \cdot 0.5 \text{ MeV}} \approx 52.9 \text{ pm},$$

or about 0.529 Angstroms. We then have a corresponding energy scale (plugging in a_0 for r into the energy)

$$\frac{e^2}{a_0} = \frac{e^4 m}{\hbar^2} = \frac{e^4}{\hbar^2 c^2} mc^2 = \alpha^2 mc^2$$

In other words, the bound state energies in this problem are on the order of α^2 of the rest energy 511 keV of the electron, which is about 27.2 eV. Half of this quantity is the potentially-familiar 13.6 eV, which is the negative of the true ground state energy of the hydrogen atom. But of course we wouldn't know that at this stage, since we're just doing dimensional analysis! And connecting this to some calculations we did at the beginning of 8.04, note that the Compton wavelength of the electron is a factor 2π off of

$$\alpha a_0 = \frac{\lambda_c}{2\pi} = \frac{\hbar}{mc} \approx 400 \text{ fm},$$

much smaller than the Bohr radius, and then we get the classical electron radius with another factor of α :

$$\alpha^2 a_0 \approx 2.8 \text{ fm}.$$

(For comparison, the size of a proton is approximately 1 fm.) With this, we now have a general scale (length and energy) for the problem we're considering, and we'll solve the Schrodinger equation for **bound states of this potential** (meaning that $E < 0$) – scattering states are usually covered in more advanced courses. This is an interesting physical problem, because we'll get the exact forms for the energy levels of a system with many applications.

Remark 142. *There are many other effects that change the energy levels of the actual hydrogen atom, such as the fine structure, relativistic effects, and so on. But those are higher order effects, and we won't discuss them for now.*

Plugging in our $V(r)$ into the **radial** Schrodinger equation, we are trying to solve for solutions to

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} - \frac{Ze^2}{r}\right) U(r) = EU(r)$$

with $E < 0$. (Remember that the solution U depends on E and ℓ , so we need to solve for the allowed energy levels for each of $\ell = 0, 1, 2, \dots$ – once we find the solutions to the differential equation, our full wavefunction will be $\psi(r, \theta, \phi) = \frac{U(r)}{r} Y_{\ell, m}(\theta, \phi)$.) Our first step will be to get rid of units and replace r by a unit-free variable – we do this by making use of the characteristic length a_0 , and it turns out the other constants will simplify best if we define

$r = \frac{a_0}{2Z} x$: skipping some of the algebra here (but using that $\frac{\hbar^2}{m} = a_0 e^2$ and that $\frac{d^2}{dr^2} = \frac{4Z^2}{a_0^2} \frac{d^2}{dx^2}$), we end up with

$$\frac{2Z^2 e^2}{a_0} \left(-\frac{d^2}{dx^2} + \frac{\ell(\ell+1)}{x^2} - \frac{1}{x}\right) U(x) = EU(x) \implies \left(-\frac{d^2}{dx^2} + \frac{\ell(\ell+1)}{x^2} - \frac{1}{x}\right) U = -\kappa^2 U,$$

which is now a unit-free equation in terms of the unit-free energy $\kappa^2 = -\frac{E}{\left(\frac{2Z^2 e^2}{a_0}\right)}$ – our goal is now to know what

values of κ give us valid solutions to the differential equation. The equation now looks a lot simpler than before, but it's still unfortunately not that easy to solve – in particular, if we try to write down a series solution with the equation in its current form, we will get a three-term recursion (which is more complicated than a two-term one).

A good strategy for simplifying is to look at the behavior of the solution near zero or near infinity – because the second and third terms on the left-hand side vanish as $x \rightarrow \infty$, the differential equation is approximately $-\frac{d^2 U}{dx^2} = -\kappa^2 U$, which is solved by $U = e^{\pm \kappa x}$ (we'll want the decaying solution for normalization reasons). This motivates us to again make a transformation $\rho = \kappa x = \frac{2\kappa Z}{a_0} r$, which turns the differential equation into

$$\left(-\frac{d^2}{d\rho^2} + \frac{\ell(\ell+1)}{\rho^2} - \frac{1}{\kappa\rho}\right) U = -U.$$

(Note that it's important that κ still shows up somewhere in this equation, since the problem we're trying to solve fundamentally involves fixing the allowed values of the energy.) And now if we look at the solution as $\rho \rightarrow 0$ (which is the same as taking r or x to 0), we know that $u \sim \rho^{\ell+1}$ from the discussion last lecture. So we know that the solutions to this equation are not polynomial (because they decay exponentially as $e^{-\kappa x} = e^{-\rho}$) and also that they don't start in the power series until $\rho^{\ell+1}$. To encode all of that information, we'll write down the ansatz

$$U(\rho) = \rho^{\ell+1} W(\rho) e^{-\rho}$$

for some unknown function $W(\rho)$, with the hope that $W(\rho)$ will be simpler than $U(\rho)$. Plugging into the boxed differential equation (which just involves a lot of algebra), we get something that initially looks like it's worse than the original:

$$\rho \frac{d^2 W}{d\rho^2} + 2(\ell+1-\rho) \frac{dW}{d\rho} + \left[\frac{1}{\kappa} - 2(\ell+1)\right] W = 0.$$

But this is actually a better equation for a **series solution**, because if we plug in $W = \rho^k$ into the left-hand side, every term ends up being proportional to either ρ^{k-1} or ρ^k , meaning that we will get a simple one-step recursion relation (given a_k , we can find a_{k+1}). So letting $W = \sum_{k=0}^{\infty} a_k \rho^k$, we can get our recursion relation by setting the total ρ^k coefficient to zero, and we find

$$\frac{a_{k+1}}{a_k} = \frac{2(k+\ell+1) - \frac{1}{\kappa}}{(k+1)(k+2\ell+2)}.$$

Looking at the limiting behavior as $\rho \rightarrow \infty$, we find that $\frac{a_{k+1}}{a_k} \sim \frac{2}{k}$. But this doesn't decay fast enough – in particular,

even if $\frac{a_{k+1}}{a_k} = \frac{2}{k+1}$ (which even decays slightly faster), we would have $a_k = \frac{2^k a_0}{k!}$, and that would give us

$$\sum_k a_k \rho^k \approx a_0 \sum \frac{2^k}{k!} e^k = a_0 e^{2\rho}.$$

And this is actually nicely consistent with what we found earlier – **if the series does not terminate**, then our solution is proportional to a polynomial factor times $e^\rho e^{-2\rho}$, which means the behavior near $\rho \rightarrow \infty$ has a $e^{+\rho}$ factor instead of an $e^{-\rho}$ one, which still solves the differential equation but just diverges.

But if we want normalizable bound states, our series must be truncated at some point. For the sake of characterizing our solutions, we'll be careful with this step: if we want W to be a polynomial of degree N , then $a_N \neq 0$ but $\frac{a_{N+1}}{a_N} = 0$ (and then $a_{N+1}, a_{N+2}, a_{N+3}, \dots$ will all automatically be zero because we have a one-step recursion problem). So then we must have

$$\frac{1}{\kappa} = 2(N + \ell + 1),$$

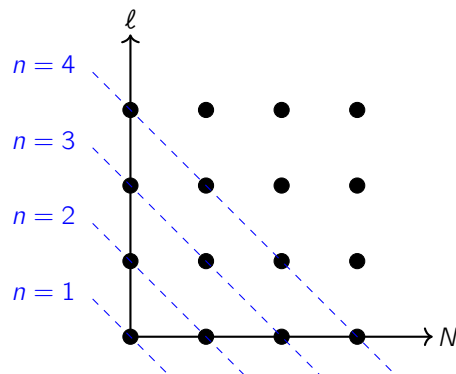
and because κ is related to the energy E , we see that the energy is quantized – it has to be the negative reciprocal of some integer! And ℓ can take on any nonnegative integer value (because that's how we set up the problem), and so can N (because it's the degree of our polynomial $W(\rho)$). But that means that **there is degeneracy in this problem** – for any given value of $N + \ell + 1$, there are many ways we can choose N and ℓ to get the correct sum. So defining the **principal quantum number**

$$n = N + \ell + 1 = \frac{1}{2\kappa},$$

which is always a positive integer, we now have a formula for the n th energy level of the hydrogen atom: rearranging the definition of κ ,

$$E_n = -\frac{2Z^2 e^2}{a_0} \kappa^2 = \boxed{-\frac{Z^2 e^2}{2a_0} \cdot \frac{1}{n^2}},$$

and we've derived the famous $\frac{1}{n^2}$ factor for the energy levels of the hydrogen atom, involving the famous constant $\frac{e^2}{2a_0} = 13.6$ eV. For visualization, if we imagine drawing all of the nonnegative integer lattice points in the (N, ℓ) -plane, then diagonally slanting lines correspond to a fixed value of n :



In general, we see that there are n possible solutions where $N + \ell + 1 = n$ (with the constraint $0 \leq \ell, N \leq n - 1$), which are $(0, n - 1), (1, n - 2), \dots, (n - 1, 0)$, and all of these solutions are at energy level E_n . But that does not mean that there is just an n -fold degeneracy, because **now we have to remember that m can range over the $(2\ell + 1)$ values from $-\ell$ to ℓ** , giving us different energy eigenstates even if we have the same function U ! So for $n = 1$, we must have $\ell = 0$, which only gives us one state. But then for $n = 2$, we can have $\ell = 1$ or $\ell = 0$, giving us $3 + 1 = 4$ states. And for $n = 3$, the allowed values are $\ell = 2, 1, 0$, corresponding to $5 + 3 + 1 = 9$ overall states – this pattern continues, and there are $\boxed{n^2}$ total states at energy level E_n . And to summarize, each state in the hydrogen atom comes with three quantum numbers, namely

- the **principal quantum number** n , which fixes the energy of the state and can be any positive integer,
- the **angular momentum quantum number** ℓ (this is more significant physically than the degree of the polynomial $N = n - \ell - 1$, so it makes sense to use this), which is a positive integer between 0 and $(n - 1)$, and
- the **magnetic quantum number** m , representing the z-component of angular momentum, which is an integer between $-\ell$ and ℓ .

Returning to the variables we've defined along the way, now that we know $\kappa = \frac{1}{2n}$, we see that

$$\rho = \frac{2\kappa Z}{a_0} r = \frac{Zr}{na_0},$$

so the full wavefunction solution in three dimensions is, up to constant factors,

$$\psi_{n,\ell,m} = \frac{U_{n,\ell}}{r} Y_{\ell,m} \sim \frac{\rho^{\ell+1}}{\rho} W_{n,\ell}(\rho) e^{-\rho} Y_{\ell,m}(\theta, \phi) = \rho^\ell W(\rho) e^{-\rho} Y_{\ell,m}(\theta, \phi)$$

where $W(\rho)$ is a polynomial of degree $N = n - \ell - 1$ (these are called the **Laguerre polynomials**). And converting back to the usual radial coordinate, we have

$$\psi_{n,\ell,m}(r, \theta, \phi) = A \left(\frac{r}{a_0} \right)^\ell \left(\text{polynomial in } \frac{r}{a_0} \text{ of degree } (n - \ell - 1) \right) e^{-Zr/(na_0)} Y_{\ell,m}(\theta, \phi)$$

for some normalization constant A . For reference, the simplest solution $\psi_{1,0,0}$ is spherically symmetric and looks like

$$\psi_{1,0,0} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

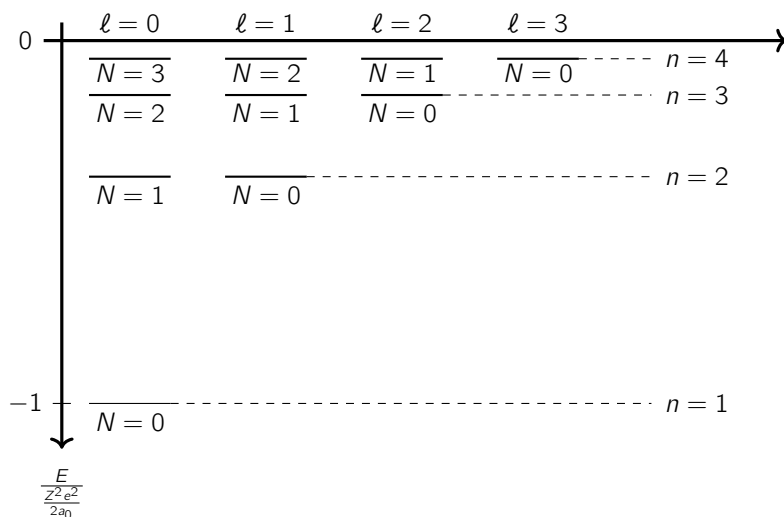
when $Z = 1$, so we now have an explicit formula for the ground state of the hydrogen atom!

Lecture 23: Spectrum, Degeneracy, and Other Properties of the Hydrogen Atom

Last lecture, we found the energy levels of the hydrogen (or hydrogen-like) atom Hamiltonian, and we found that we can describe the eigenstates $\psi_{n,\ell,m}$ with three quantum numbers, where the principal quantum number n tells us the energy $E_n = -\frac{Z^2 e^2}{2a_0 n^2}$ of the state, the angular momentum quantum number $0 \leq \ell \leq n - 1$ tells us the total angular momentum of the state, and the magnetic quantum number $-\ell \leq m \leq \ell$ tells us the state's angular momentum in the z-direction. And the wavefunction itself (in spherical coordinates) consists of a product of a normalization factor, a $\left(\frac{r}{a_0}\right)^\ell$ term (behavior as $r \rightarrow 0$), a Laguerre polynomial in $\frac{r}{a_0}$ of degree $(n - \ell - 1)$, an exponential decay $e^{-Zr/(na_0)}$ (behavior as $r \rightarrow \infty$), and a spherical harmonic $Y_{\ell,m}$.

Remark 143. *Only very detailed calculations will actually require us to know the specific polynomial terms, so we won't talk much about it here. And it's often faster to just do the recursion relation calculation, rather than trying to search up the wavefunction and figure out discrepancies between units and conventions.*

It turns out that there's a classic way to draw the energy levels of bound states for a central potential, in which we represent energy on the y-axis and ℓ on the x-axis. We'll use units of $\frac{E}{\frac{Z^2 e^2}{2a_0}}$ for our system, so that the energies are at $-\frac{1}{n^2}$ for positive integers n – the diagram below is not drawn exactly to scale because the energy levels would be much more squashed near $E = 0$:



Basically, each dash represents a different E and ℓ for which we have an energy eigenstate, so each column essentially corresponds to a different differential equation (because the effective potential changes depending on the value of ℓ). And for our system, incrementing n by one means that we have a state at energy E_n in a new column (specifically $\ell = n - 1$), and N always ranges from $(n - 1)$ to 0 within any row.

But there's more that we can say: for any given column (that is, any particular value of ℓ), it makes sense that the lowest energy state has $N = 0$, and the next energy state has $N = 1$, and so on, because the **node theorem** for a one-dimensional potential (the radial equation for any given ℓ) tells us that the ground state has no nodes, the next state has one node, and so on, and the only term in $\psi_{n,\ell,m}$ that can vanish is this polynomial. (Here, behavior at $r = 0$ doesn't count because that's the boundary of the wavefunction, which doesn't count as a node.) So the incrementing values of N should not be surprising to us, and in fact we learn that the Laguerre polynomials of degree N must have N distinct real zeros.

On the other hand, the degeneracy **across** values of ℓ is extraordinary and very special to this problem! Usually, when we solve the radial equations for $\ell = 0, 1, 2, \dots$, we will get different energy levels for each of those problems, but there is no reason a priori that the energy levels should actually line up for the hydrogen atom (and do so in such an organized way). We do expect some degeneracy to always be present – for example, each line above in the $\ell = 2$ column really corresponds to a multiplet of five states with $m = 2, 1, 0, -1, -2$ – but the additional degeneracy between different ℓ s is very special and is not explained by any of the theory we've discussed in this class so far.

Fact 144

This fact led to developments with the **Runge-Lenz vector**, which is a conserved vector in planetary orbits in Newton's theory. Precession of elliptical orbits is not allowed under Newton's theory (though it is under Einstein's theory of relativity), so it is not allowed for the hydrogen atom, and in fact that is connected to why we have all of these hidden degeneracies.

For comparison, if we had instead solved the **infinite spherical well** problem (which we do in 8.05), in which the potential is zero inside a sphere and infinite outside, we do not see the coincidences in energy levels between different ℓ s, even though the potential looks very simple in that case. The point to take away here is that this kind of hydrogen atom behavior can only be explained by an **extra symmetry**!

Example 145

For some intuition, we'll start with the $Z = 1$ ground state, $\psi_{1,0,0} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$, and understand how to obtain the general- Z ground state without much additional work.

Remembering that the potential $V(r)$ goes from $-\frac{e^2}{r}$ to $-\frac{Ze^2}{r}$ when we go from 1 to Z protons, we should substitute e^2 with Ze^2 everywhere in our wavefunction. And because $a_0 = \frac{\hbar^2}{me^2}$, this means that we should replace a_0 with $\frac{a_0}{Z}$ everywhere as well. (Often we write solutions in a "mixed way" involving both e and a_0 , so we should make sure to make both changes.) So in this case, the ground state wavefunction for a general hydrogen-like atom is

$$\psi_{1,0,0}(r, \theta, \phi) = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Zr/a_0}.$$

(Intuitively, the fact that the "normalization did not care about a_0 appearing in the wavefunction" means that if we replace a_0 with any other constant, in this case $\frac{a_0}{Z}$, we will still have a normalized wavefunction.) And we've discussed this before in slightly different words, but the reason for the $\frac{Zr}{a_0}$ factor in the exponential is that the two of the terms in the radial differential equation go to zero as $r \rightarrow \infty$, leaving just $-\frac{\hbar^2}{2m} \frac{d^2U}{dr^2} = EU$. This should have solutions proportional to $e^{\pm\sqrt{2mE/\hbar^2}r}$, and plugging in the value of E_1 (or E_n in general) indeed recovers the correct exponential decay for the ground state.

We can now turn our attention to another aspect of the hydrogen atom:

Definition 146

A **Rydberg atom** is an atom where the outermost electron is in a very high principal quantum number n .

In such a setting, we can imagine having a nucleus of charge Ze , a lot of electrons around it, and then the last electron sees the charge from both the nucleus and the $(Z - 1)$ other electrons. So essentially by Gauss's law, the outermost electron (if it's outside the shell of the remaining electrons) sees an overall charge of $+1$. (It can be checked that the electrons do appear further and further away from the nucleus for higher n , so this argument is basically valid.) So to a good approximation, a Rydberg atom behaves a lot like a hydrogen atom.

A good first step is for us to calculate the **size of a Rydberg atom** (this doesn't really make sense precisely, but we can ask for the **expectation of the radius**), and it turns out the answer is not actually a constant factor times na_0 , even though the exponential factor in the wavefunction is $e^{-r/(na_0)}$. Instead, the intuitive explanation will come from the **virial theorem**:

Theorem 147 (Virial theorem)

For the hydrogen atom (or any potential proportional to $\frac{1}{r}$), we have

$$\langle T \rangle = -\frac{1}{2} \langle V \rangle$$

where T is the kinetic energy and V is the potential energy.

(We won't prove this theorem for now, but it involves some algebraic calculations with commutators.) We can picture this as saying that the kinetic energy $\langle T \rangle$ and the bound state energy $E_b = \langle T \rangle + \langle V \rangle$ are negatives of each other, since $\langle V \rangle = -2\langle T \rangle$. That means that $\langle V \rangle = 2E_b$, or for the Rydberg atom we're discussing (for which $Z = 1$ as discussed),

$$\left\langle -\frac{e^2}{r} \right\rangle = 2E_b = 2 \left(-\frac{e^2}{a_0 n^2} \right) \implies \left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a_0}.$$

So this suggests that the typical radius is actually on the order of $\boxed{n^2 a_0}$ instead of na_0 . Everything we've discussed above is exact, but note that $\langle \frac{1}{r} \rangle = \frac{1}{n^2 a_0}$ does not imply that $\langle r \rangle = n^2 a_0$ (we can't manipulate expectation values that way). In fact, the expectation of r actually depends on ℓ , and it can be calculated with a bit more effort to be

$$\langle r \rangle = n^2 a_0 \left[1 + \frac{1}{2} \left(1 - \frac{\ell(\ell+1)}{n^2} \right) \right].$$

(In particular, this expectation is $\frac{3}{2}n^2 a_0$ for $\ell = 0$ and approximately $n^2 a_0$ for $\ell = (n-1)$.) And now we can look back at the wavefunction to understand where this n^2 factor comes from: our solution is of the form

$$\psi_{n,\ell,m} = A r^\ell W_{n,\ell}(r) e^{-r/(na_0)} Y_{\ell,m}(\theta, \phi) = f_{n,\ell}(r) Y_{\ell,m}(\Omega),$$

where $f_{n,\ell}$ is a polynomial of degree $(n-\ell-1) + \ell = n-1$ times an exponential factor. So the probability density of finding the radius to be between r and $r+dr$ is

$$p(r)dr = r^2 dr \int |\psi|^2 d\Omega = r^2 dr |f_{n,\ell}|^2 \int |Y_{\ell,m}|^2 d\Omega$$

(since we need to integrate out $|\psi|^2 d^3x$ along the angular coordinates). But by definition of the spherical harmonics, the integral over solid angle is 1, and then cancelling the dr s gives us the **radial probability density**

$$p(r) = r^2 |f_{n,\ell}|^2.$$

And it is the polynomial factor that is causing us trouble here – since $f_{n,\ell}$ contains a degree $(n-1)$ polynomial, let's just keep the leading order term r^{n-1} and say that $f_{n,\ell}(r) \sim r^{n-1} e^{-r/(na_0)}$, so that (plugging back in)

$$p(r) \sim r^{2n} e^{-2r/(na_0)}.$$

So there is a "fight" between the exponential and the polynomial factor in the probability density – since r^{2n} is increasing and $e^{-r/(na_0)}$ is decreasing, their product will basically be sharply peaked, and it will be have a maximum where the derivative $p'(r)$ is zero:

$$0 = p'(r) = \left(\frac{2n}{r} - \frac{2}{na_0} \right) r^{2n} e^{-r/(na_0)} \implies r = n^2 a_0,$$

giving us the expected n^2 dependence for the radius!

Example 148

Rydberg atoms can be observed in nature in interstellar gases – during **recombination**, when protons capture electrons to form atoms while the universe cooled down, they may capture the electron at a high quantum number.

In astrophysics, $n = 350$ has been measured, which means that the size of the Rydberg atom is about $350^2 a_0 \approx 6.5 \mu\text{m}$. This size is on the order of the size of a red blood cell (which is about $8 \mu\text{m}$) and just a bit smaller than the diameter of a hair (which is about $50 \mu\text{m}$). Also, these atoms are relatively stable – while an electron in the $n = 5$ energy state would jump to $n = 1$ within about 10^{-7} seconds, these Rydberg atoms with very high n sometimes last a millisecond or a tenth of a second (because it takes a long time to spiral down the energy levels when the distance between them is on the order of $\frac{1}{n^3}$).

These atoms can be created using lasers in the lab, and they can be detected using ionization (because the energy required to ionize these atoms is much smaller than those for ordinary atoms). In other words, Rydberg atoms are **semiclassical**, and in fact Bohr's calculations of the energy levels of the hydrogen atom (which were correct) didn't

require quantum mechanical derivations – he just needed to assume quantization on the allowed photons emitted during energy transitions.

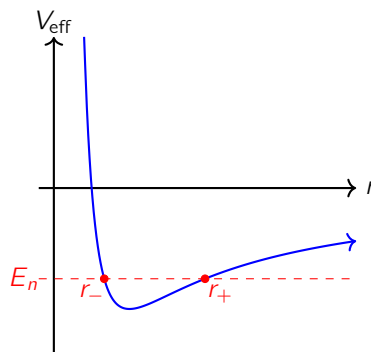
Example 149

We'll finish this lecture by discussing the effect of the **effective potential** in more detail – specifically, we'll consider a large n (like 100) and see what happens to the **orbit of the electron** as ℓ varies.

Initially, we might think that $\ell = 0$ will be the most circular out of the different states (because it's spherically symmetric), but in fact it will be the most elliptical (and $\ell = 99$ is the most circular). The intuition is as follows: the effective potential for the radial equation is

$$V_{\text{eff}} = \frac{\hbar\ell(\ell + 1)}{2mr^2} - \frac{e^2}{r},$$

which looks roughly as shown below (with $\frac{1}{r}$ dominating for large r and $\frac{1}{r^2}$ dominating for small r):



If we then imagine a particle at energy E_n rolling around in this potential, we get a more elliptical orbit if the **distance between the two endpoints** r_+ and r_- (where $V_{\text{eff}}(r) = E_n$) is larger. (After all, if we imagine a planetary orbit, the most elliptical orbits get very close and very far away from the sun, and the most circular ones have a constant r throughout the whole orbit.) So when $\ell = 0$, because we don't even have the upward behavior in the V_{eff} graph as $r \rightarrow 0$, the electron reaches all the way to $r = 0$ and we have the largest possible orbit. And when ℓ gets larger and larger, the $\frac{\hbar\ell(\ell+1)}{2mr^2}$ factor will push the blue curve higher and higher, making the endpoints closer and closer. So we get the most circular orbit when V_{eff} is almost tangent to the horizontal line at E_n , and that comes from the top value of $\ell = n - 1$.

For another way of thinking about this, circular orbits do in fact have a lot of angular momentum $\vec{r} \times \vec{p}$ (because the two vectors are orthogonal), but elliptical orbits do not because the angle between \vec{r} and \vec{p} is very small when the particle is far from the center. And next lecture, we'll do some more calculations with r_+ and r_- to understand how they relate to the elliptical orbit, but the punchline is that $\frac{r_+ + r_-}{2} = n^2 a_0$ regardless of the value of ℓ ! So in our hydrogen atom spectrum that we drew in the beginning of this lecture, we should think of the energy states of the same n as elliptical orbits of different eccentricity. And this connects to Kepler's discovery that the total period of an orbit depends only on $r_- + r_+$, the major diameter of the ellipse, meaning that ellipses of the same major diameter have the same energy.

Lecture 24: Hydrogen Atom and Spin Angular Momentum

Last lecture, we drew the spectrum of the hydrogen atom (which, for central potentials in general, involves drawing the energy levels for the various bound states in different columns for $\ell = 0, 1, 2$, and so on). For a generic central

potential $V(r)$, solving the Schrodinger equation for the various effective potentials $V_{\text{eff}}(r) = V(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}$ involves solving a bunch of different differential equations, and there is no reason that the energy levels will line up. But in the hydrogen atom, a special symmetry happens to make the energy levels very degenerate (even beyond the $(2\ell + 1)$ -fold degeneracy coming from the different values of m we can have for each (n, ℓ)).

At the end of the discussion, we started analyzing the various orbits of the hydrogen atom for a fixed n (which is where our “semi-classical” arguments are more valid). In such a situation, we can imagine that our electron is making elliptical orbits around the proton, and the r_- and r_+ from the diagram below Example 149 correspond to the shortest and longest distance to the proton, which together make up the major axis of the ellipse. (Classically, we can imagine that the electron is oscillating between r_- and r_+ . But quantum mechanically – and thus more accurately – we have a wavefunction $|\psi|^2$ which is exponentially decaying outside of the region $[r_-, r_+]$, and the probability density will mimic the time spent at various r s in an elliptical orbit.)

Example 150

We claimed last lecture that the “turning points” where $V_{\text{eff}}(r) = E_n$ satisfy $\frac{r_- + r_+}{2} = n^2 a_0$, and we’ll verify that fact now with an explicit calculation.

Plugging in the formulas for the energy levels and the effective potential, we have

$$\frac{\hbar^2 \ell(\ell + 1)}{2mr^2} - \frac{e^2}{r} = -\frac{e^2}{2a_0} \frac{1}{n^2}.$$

This is a quadratic equation in r , but we can do a transformation $r = a_0 x$ to get the equation

$$\frac{\hbar^2 \ell(\ell + 1)}{2ma_0^2} \frac{1}{x^2} - \frac{e^2}{a_0 x} = -\frac{e^2}{2a_0 n^2},$$

but now $\frac{\hbar^2}{2ma_0^2} = \frac{\hbar^2}{2ma_0} \cdot \frac{1}{a_0} = \frac{\hbar^2}{2ma_0} \cdot \frac{me^2}{\hbar^2} = \frac{e^2}{2a_0}$, so all of the $\frac{e^2}{2a_0}$ factors cancel out and we’re left with

$$\frac{\ell(\ell + 1)}{x^2} - \frac{2}{x} = -\frac{1}{n^2} \implies \frac{1}{x} = \frac{1 \pm \sqrt{1 - \frac{\ell(\ell+1)}{n^2}}}{\ell(\ell + 1)}$$

by the quadratic formula (treating $\frac{1}{x}$ as the variable). We thus get the two solutions

$$x = \frac{\ell(\ell + 1)}{1 \pm \sqrt{1 - \frac{\ell(\ell+1)}{n^2}}} = \frac{\ell(\ell + 1) \left(1 \mp \sqrt{1 - \frac{\ell(\ell+1)}{n^2}} \right)}{1 - \left(1 - \frac{\ell(\ell+1)}{n^2} \right)} = \boxed{n^2 \left(1 \mp \sqrt{1 - \frac{\ell(\ell + 1)}{n^2}} \right)}$$

by rationalizing the denominator (multiplying numerator and denominator by the radical conjugate), and thus r_+ and r_- are just a_0 times those two solutions. And indeed, the \pm factor cancels out, and $r_+ + r_- = 2a_0 n^2$, recovering the result from last lecture. Furthermore, $r_+ \approx r_-$ when ℓ is large, because the additional \pm term is close to zero in that case, and $r_- = 0$ and $r_+ = 2n^2 a_0$ when ℓ is zero, giving us the most elliptical orbit. (But because this is still a semi-classical argument, the idea of an “orbit” is not so accurate at the extreme values.) For a numerical example, in a typical Rydberg atom with $n = 100$ and $\ell = 60$, we have $r_+ \approx 18000a_0$ and $r_- \approx 2000a_0$, but every other state with $n = 100$ will also have $r_+ + r_- = 20000$.

Example 151

To finish the course, we’ll turn our attention to motivating **spin angular momentum** and the mathematical treatment of spin by considering the “simplest quantum system.”

We might initially say that the simplest quantum system is the particle in the box, but that system has infinitely many energy eigenstates, each of which is a function on an interval. And even states with only one bound state, like the delta potential, may have infinitely many scattering states, which are still complicated to deal with.

So we'll go back to the Schrodinger equation $i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi$, for which we can solve for energy eigenstates of the form $e^{-iEt/\hbar}\psi$ and thus only need to solve the equation $\hat{H}\psi = E\psi$. Picking a quantum system then comes down to picking our Hamiltonian \hat{H} , which can be any Hermitian operator with units of energy (which requires defining an inner product). We've been solving these kinds of equations in this class when ψ represents a particle living in one dimension (as motivated by classical mechanics), but such wavefunctions take on uncountably many values. So the key to simplifying our system is to be less attached to the physics for a while.

What we'll do is assume that we have a particle which can only live at **one of two points** x_1 or x_2 , rather than on the whole real line. (It's not interesting if the particle can only be at one point, because then the probability of finding it there is just one.) So instead of having $\psi(x)$ be a function on the real numbers, we can just think of ψ as having the two pieces of information (which we'll encode in a vector) $\begin{bmatrix} \psi(x_1) \\ \psi(x_2) \end{bmatrix} = \begin{bmatrix} \alpha \\ \beta \end{bmatrix}$. The probability of finding the particle at position x_1 is then $|\alpha|^2$, and the probability of finding it at x_2 is $|\beta|^2$.

Fact 152

This setting may look familiar from our discussion with interferometers back in the second lecture of this class! But such a vector can also encode information about other systems, such as a particle which can either be on the left or right side of a box with a partition. And it can also encode a situation where a particle is in one of **two states**, either "spin down" or "spin up" – that's what we're moving toward right now.

Such two-state systems turn out to be very rich mathematically – to see this, we need to start by constructing the inner product. Instead of the usual integral $(\phi, \psi) = \int \phi^*(x)\psi(x)dx$, in which we're basically adding up the contributions of $\phi^*\psi$, it is natural now to have the inner product be

$$\psi_1 = \begin{bmatrix} \alpha_1 \\ \beta_1 \end{bmatrix}, \quad \psi_2 = \begin{bmatrix} \alpha_2 \\ \beta_2 \end{bmatrix} \implies (\psi_1, \psi_2) = \alpha_1^*\alpha_2 + \beta_1^*\beta_2.$$

In other words, we can think of taking the conjugate transpose of the vector for ψ_1 and performing matrix multiplication:

$$(\psi_1, \psi_2) = \begin{bmatrix} \alpha_1^* & \beta_1^* \end{bmatrix} \begin{bmatrix} \alpha_2 \\ \beta_2 \end{bmatrix}$$

(And as we might explore in a future class, we can also think of a wavefunction $\psi(x)$ for a one-dimensional particle as an infinite column vector of values $\dots, \psi(-\epsilon), \psi(0), \psi(\epsilon), \psi(2\epsilon), \dots$.) If we now think of \hat{H} as a 2×2 matrix acting on these column vectors by matrix multiplication, the condition for being Hermitian is that $(H^T)^* = H$ (we can check this by a direct calculation, but we can think of it as coming from the fact that we are transposing and complex conjugating ψ_1 in the definition of the inner product.)

The power of this setup will now become clear as we try to classify all Hamiltonians for this two-state system. A 2×2 matrix equal to its conjugate transpose must have real entries on the diagonal, and the other two entries must be complex conjugates, so the most general Hamiltonian is

$$\hat{H} = \begin{bmatrix} a_0 + a_3 & a_1 - ia_2 \\ a_1 + ia_2 & a_0 - a_3 \end{bmatrix},$$

where a_0, a_1, a_2, a_3 are **real** numbers. (We've chosen to represent the two diagonal entries in this way for reasons that

will become clear soon, but we can check that we can indeed pick a_0 and a_3 to get any real entries on the diagonal.) We can then rewrite this matrix as

$$\hat{H} = a_0 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + a_1 \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} + a_2 \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} + \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}.$$

The four matrices on the right-hand side are the four basic Hermitian 2×2 matrices – scaling them by real numbers and adding them together still gives us a Hermitian matrix. In other words, we can say that there is a **four-dimensional space** of matrices, spanned by these four basic matrices. They are so important that we give them names – the first one is the 2×2 identity matrix, and the next three are called the **Pauli matrices** σ_1 , σ_2 , and σ_3 , respectively.

If we want to write a Hamiltonian down for a physical system, though, we need \hat{H} to have units of energy. And there really isn't a reason to use the identity matrix, because that's like adding a constant to the Hamiltonian, which doesn't change the calculations or the states. (For example, we saw this in the harmonic oscillator, whose Hamiltonian was $\hat{H} = \hbar\omega (\hat{N} + \frac{1}{2})$, but for which we could just work with \hat{N} instead.) Since $\hbar\omega$ has units of energy, the Hamiltonian we'll write down here is

$$\hat{H} = \frac{\hbar\omega_1}{2}\sigma_1 + \frac{\hbar\omega_2}{2}\sigma_2 + \frac{\hbar\omega_3}{2}\sigma_3$$

(the factors of 2 will be clear soon) for some real numbers $\omega_1, \omega_2, \omega_3$. Rewriting this slightly as

$$\hat{H} = \omega_1 \left(\frac{\hbar}{2}\sigma_1 \right) + \omega_2 \left(\frac{\hbar}{2}\sigma_2 \right) + \omega_3 \left(\frac{\hbar}{2}\sigma_3 \right),$$

we see that the three terms in parentheses have units of angular momentum, so we may hope that there is something to do with angular momentum in this setup! Specifically, it is reasonable to try defining the operators

$$\hat{S}_x = \frac{\hbar}{2}\sigma_1, \quad \hat{S}_y = \frac{\hbar}{2}\sigma_2, \quad \hat{S}_z = \frac{\hbar}{2}\sigma_3$$

as potential components of angular momentum. And in fact, the commutators here are easy to compute because we have matrices:

$$\begin{aligned} [\hat{S}_x, \hat{S}_y] &= \left[\frac{\hbar}{2}\sigma_1, \frac{\hbar}{2}\sigma_2 \right] = \frac{\hbar}{2} \cdot \frac{\hbar}{2} \left(\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} - \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \right) \\ &= \frac{\hbar}{2} \cdot \frac{\hbar}{2} \left(\begin{bmatrix} i & 0 \\ 0 & -i \end{bmatrix} - \begin{bmatrix} -i & 0 \\ 0 & i \end{bmatrix} \right) \\ &= \frac{\hbar}{2} \cdot \frac{\hbar}{2} \begin{bmatrix} 2i & 0 \\ 0 & -2i \end{bmatrix} \\ &= i\hbar \cdot \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \\ &= i\hbar \frac{\hbar}{2}\sigma_z = \boxed{i\hbar\hat{S}_z}. \end{aligned}$$

So we have the same commutation relation as with the angular momentum operators $\hat{L}_x, \hat{L}_y, \hat{L}_z$ from a few lectures ago – not only do the \hat{S} operators have the same units as angular momentum, but they also have the correct commutators (we can check that $[\hat{S}_y, \hat{S}_z] = i\hbar\hat{S}_x$ and that $[\hat{S}_z, \hat{S}_x] = i\hbar\hat{S}_y$ as well). So angular momentum does not actually require complicated operators involving \vec{r} and \vec{p} – we can construct it with just 2×2 matrices. And what we've created is **spin one-half**, the angular momentum coming from having two discrete degrees of freedom – it's really a mathematical object, but the interpretation of “spin up” and “spin down” came from physicists.

This system is the setting for a substantial fraction of the material of 8.05 – it turns out that the physical

interpretation takes some getting used to. Looking back at the Hamiltonian

$$\hat{H} = \omega_1 \hat{S}_x + \omega_2 \hat{S}_y + \omega_3 \hat{S}_z = \vec{\omega} \cdot \hat{S},$$

where $\vec{\omega}$ is a vector of real numbers and $\hat{S} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)$, it turns out this Hamiltonian actually represents **a spin in a magnetic field**, and solving the corresponding Schrodinger equation will reveal that the spin will precess in the magnetic field – this is the origin of NMR (nuclear magnetic resonance), which is used to detect the density of fluids in the body.

Looking ahead to 8.05, we'll conclude by mentioning some properties of the eigenstates of \hat{H} . Recall that for our previous angular momentum problem, we measured the eigenvalues for \hat{L}^2 and \hat{L}_z . Similarly, we'll measure the eigenvalues for \hat{S}^2 and \hat{S}_z here, where \hat{S}_z represents **the spin in the z-direction**. Because \hat{S}_z is the matrix $\frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$, which is a diagonal matrix, its eigenvectors are

$$|\uparrow\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad |\downarrow\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

(here “up” and “down” arrows represent being in the upper or lower component), where the eigenvalues are $\frac{\hbar}{2}$ and $-\frac{\hbar}{2}$, respectively:

$$\hat{S}_z |\uparrow\rangle = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{\hbar}{2} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{\hbar}{2} |\uparrow\rangle, \quad \hat{S}_z |\downarrow\rangle = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = -\frac{\hbar}{2} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = -\frac{\hbar}{2} |\downarrow\rangle.$$

And the reason for the name of “spin one-half” is that we have the factor of 2 in the eigenvalues and operators that we've defined – it might look like that choice was arbitrary, but in fact it was **necessary** to make the angular momentum commutators work out! In other words, two-state systems are forced to be spin one-half, and such systems must have angular momentum measured to be either $\frac{\hbar}{2}$ or $-\frac{\hbar}{2}$. (In contrast, a photon is an example of a spin-one system, in which the two directions of circular polarization correspond to a spin of \hbar or $-\hbar$.)

But now that we know what spins look like along the z-direction, we may also be curious about what spin states look like along the x- or y-direction. It may look like we're running out of states, because we only have a two-dimensional space of possible states and there are three directions of spins that we're trying to represent. And in fact, the z-spin-up and z-spin-down states were already constructed to be orthogonal and form a full basis of the vector space: any state $\begin{bmatrix} a \\ b \end{bmatrix}$ is a superposition $a |\uparrow\rangle + b |\downarrow\rangle$ of those two states. But that's not actually a problem: the operator $\hat{S}_x = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$ does have two different eigenvectors. Specifically, if we consider the (normalized) state

$$\frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix} = \frac{1}{\sqrt{2}} (|\uparrow\rangle + |\downarrow\rangle),$$

we see that

$$\hat{S}_x \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix} = \frac{\hbar}{2} \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 1 \end{bmatrix} = \frac{\hbar}{2} \cdot \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix},$$

and we do have an eigenstate of \hat{S}_x of eigenvalue $\frac{\hbar}{2}$ (which we'll denote $|\uparrow; x\rangle$), formed by taking a superposition of $|\uparrow\rangle$ and $|\downarrow\rangle$! Similarly, the state $|\downarrow; x\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix} = \frac{1}{\sqrt{2}} (|\uparrow\rangle - |\downarrow\rangle)$ will be an eigenstate of \hat{S}_x with eigenvalue $-\frac{\hbar}{2}$.

Finally, if we turn our attention to the spin states along the y-direction, we will also be able to construct eigenvectors

of \hat{S}_y . Specifically, the state

$$\frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ i \end{bmatrix} = \frac{1}{\sqrt{2}}(|\uparrow\rangle + i|\downarrow\rangle)$$

satisfies

$$\hat{S}_y \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ i \end{bmatrix} = \frac{\hbar}{2} \cdot \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \begin{bmatrix} 1 \\ i \end{bmatrix} = \frac{\hbar}{2} \cdot \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ i \end{bmatrix},$$

meaning that we have an eigenstate $|\uparrow; y\rangle$ of \hat{S}_y of eigenvalue $\frac{\hbar}{2}$, and a similar calculation shows that the state $\frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -i \end{bmatrix}$ is the eigenstate $|\downarrow; y\rangle$ of eigenvalue $-\frac{\hbar}{2}$. So complex numbers play an important role here – there would be no way to get an eigenstate for all directions otherwise.

Importantly, all of these eigenstates have nothing to do with our usual functions of x, r, θ, ϕ , and so on – spin is its own thing with finitely many degrees of freedom and column vectors as wavefunctions. But within this system, we have angular momentum, and this angular momentum is what we use to describe the spins of particles. And spin systems will play a central role in 8.05 – they'll be used to understand superposition, entanglement, Bell's inequality, and much more.